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WIRE AND CABLE INSULATING MATERIALS WITH POLYVINYL CHLORIDE AS BASE

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The non-inflammability and much greater durability of certain plastic materials, especially those based on polyvinyl chloride, are the main reasons why these are being preferred more and more, over rubber and textiles, for insulating electrical conductors. Connecting leads insulated with these plastics are already being used on a large scale for radio and other electrical apparatus. In several countries, among which the U.S.A., large quantities of wire insulated with plastic material are also being used for permanent electrical installations in houses. In some other countries the application of these new materials is hindered by the insulation resistance requirements of official testing specifications. These requirements are based on the properties of rubber; polyvinyl chloride plastics have a lower insulation resistance, which, however, is quite high enough for almost all practical purposes. It would be regretted if the good properties of these new insulating materials could not be utilized to best advantage merely on account of the lack of suitable testing specifications.

Introduction

As insulating material for electrical conductors, rubber — either alone or in combination with a textile, such as cotton — still holds a predominating position. For many years it could indeed lay claim to being the most suitable material for this purpose: it has a very high insulation resistance, is easily processed and is not costly. Certain unfavourable properties, such as its inflammability and its lack of resistance to high temperatures and ultra-violet rays, have had to be accepted. Its inflammability, in particular, is a serious limitation: faults in electrical wiring rank second on the list of the causes of fires breaking out in houses ! It is not surprising, therefore, that materials possessing better properties than rubber should have been sought, and it is even less surprising that they should have been sought in the first place among plastics, of which in the last 20 years an enormous number of different kinds with a great variety of properties have been developed. This development, it may be remarked, has been stimulated more by the threat of war in the thirties, which made it necessary to reckon with a severe shortage of rubber in all industrial countries, rather than by the desire for a better material.

As a consequence a number of plastic insulating materials have been developed which are characterised by the common feature that they are all based upon the synthetic resin polyvinyl chloride as main ingredient, with certain admixtures designated according to their effect as plasticizers, stabilizers, pigments, etc., which will be dealt with farther on. The properties of these PVC materials [1]) depend very largely upon the nature and quantities of these admixtures, and it is possible to produce, even within this limited range of plastics, a series of materials each combining certain favourable properties.

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*) Pope's Wire and Lamp Works, Venlo, Holland.

[1]) The abbreviation PVC is used in this article to denote the insulating materials based on polyvinyl chloride (thus including the admixtures); where the word polyvinyl chloride is written in full this relates to the synthetic resin itself.

In this way insulating materials have been manufactured which in many respects are far superior to rubber and are therefore being used more and more in preference to rubber. Nevertheless many are still averse to using PVC materials, mainly for one of the following reasons:

1) PVC is thought to be only a substitute for rubber, and as such only to have served its purpose under the exigencies of war.

2) It is considered that by no means sufficient experience has been obtained with PVC as insulating material, so that its use on a large scale would be too risky.

The first belief may be explained by the fact that during the war (and even for some time after it) there was a great scarcity of good plasticizers. The poor reputation of many of the PVC materials manufactured during that period (brittleness, stickiness and poor insulation) apparently still persists. At the present time, however, there is ample production of good plasticizers and results are now being obtained which ten years ago were considered to be impossible. Any fear of inferior quality is therefore now quite unjustified.

As regards the second point, i.e. the supposed lack of experience, extensive investigations were carried out both in America and in Germany even before 1940. As an example may be mentioned a test carried out in America with a PVC-insulated cable laid, without any other protection, 30 cm deep in the ground, and carrying continuously a voltage of 115 V. After twelve years the properties of the PVC material were still such that the cable could have rendered many more years' service. Data collected in Germany about PVC materials come mainly from the postal authorities, who report satisfactory results both with underground cables (laid in 1935) and with PVC wires used in telephone exchanges, notwithstanding the fact that the PVC materials used there were not so good as those used in America.

Experience on a very much wider scale has been gained during the wan. Results with PVC on ships of the U.S.Navy, where particularly strict non-inflammability requirements had to be met, were so satisfactory that it was decided to use wire insulated with this material also for the permanent electric wiring of houses. The fact that it stands up against mechanical wear, strong sunlight and moisture has been particularly demonstrated by the use of PVC for field telephone lines run out along the ground, often across rough country and in a tropical climate.

Prejudice against PVC materials is in some cases also due to the lack of understanding that any material, whatever it may be, has to be used in a manner appropriate to its properties. It is, for example, often overlooked that PVC is thermoplastic, that is to say it becomes plastic above a certain temperature, so that any mechanical pressure accompanied by too high a temperature may cause short-circuiting. If simple precautions are taken this danger can usually be avoided, but if through ignorance or negligence it is omitted to take such measures then there is a chance of PVC unjustifiably getting a bad name.

The purpose of this article is to give more publicity to the properties and characteristic features of PVC materials, and in particular those of the PVC products being manufactured by Pope's Wire and Lamp Works in Holland since before 1940 and marketed under the trade name "Podur".

The composition of PVC materials

As already stated, for the manufacture of insulating materials with polyvinyl chloride as a base a number of substances are added, each for a particular function, which will be explained below. Roughly speaking, the composition of a PVC mixture is:

	parts by weight
1. polyvinyl chloride	100
2. plasticizer(s)	30 - 80
3. stabilizers	1 - 10
4. pigments	0.1 - 2
5. fillers.	0 - 20
6. lubricants.	0.5 - 2

Polyvinyl chloride

Pure polyvinyl chloride is a white powder obtained by the polymerization [2] of vinyl chloride, $CH_2 = CHCl$. There are various methods of producing vinyl chloride. In the Netherlands a method is applied starting from ethylene (obtained from the mineral oil or coal industries) and chlorine (from the salt industry), with the formation of 1,2-dichloro ethane in an intermediate stage:

$$\underset{\text{ethylene}}{CH_2 = CH_2} + \underset{\text{chlorine}}{Cl_2} \rightarrow \underset{\text{1,2-dichloro ethane}}{CH_2Cl - CH_2Cl},$$

$$\underset{\text{1,2 dichloro ethane}}{CH_2Cl - C_2HCl} \rightarrow \underset{\text{vinyl chloride}}{CH_2 = CHCl} + \underset{\text{hydrochloric acid}}{HCl}.$$

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[2] See, e.g., J. C. Derksen and M. Stel, Plastics and their application in the electrotechnical industry, Philips Techn. Rev. 11, pp 33-41, 1949 (No. 2), in particular p. 35.

In the second stage of this process pyrolysis is applied (decomposition by heating).

The vinyl chloride obtained, which under atmospheric pressure and at room temperature is a gas but in this process is liquefied under pressure, is purified and then polymerized, when numerous monomer molecules (molecular weight 62.5) link up into long threadlike molecules with a molecular weight between 10,000 and 20,000. This means that 150 to 300 vinyl chloride molecules combine. A fully stretched molecule of polyvinyl chloride may reach a length of 0.08 μ.

This polymerization, which takes place very readily, is accelerated by catalysts (promoters), for instance benzoyl peroxide or hydrogen peroxide. It is exothermic, the large amount of heat released by the reaction (1300 calories per gram molecule of vinyl chloride) having to be carried off, because the temperature has to be kept within narrow limits, in order to obtain a constant product. Technically this can only be done properly by polymerizing in an aqueous emulsion, each dispersed droplet of vinyl chloride being surrounded by a quantity of water acting as a cooling agent. Moreover this method has the advantage that the polyvinyl chloride can thereby be obtained in a form resembling rubber latex, which lends itself well to further processing. Polyvinyl chloride latex is easily coagulated with certain agents, and, properly applied, this method results in the production of polyvinyl chloride in the form of a powder, which is easy to wash and dry. The latex can also be processed as such.

Plasticizers

Polyvinyl chloride obtained in the manner described in the form of a white powder is thermoplastic. By a combination of heat and pressure it can be formed into a horny substance, but there are very few uses for which this is suitable. When it is desired to manufacture materials resembling rubber a concentrated solution has to be made of polyvinyl chloride in non-volatile, usually liquid, solvents, which are called plasticizers or softeners.

The preparation of the solution, which is actually not liquid but rather like a gel, is called gelatinizing. This takes place at an elevated temperature (150 to 170 °C), either between pairs of rolls rotating at different speeds or in a powerful kneading machine followed by sheeting out. In both cases the gelatinized mixture is produced in the form of a sheet of 2 to 4 mm thickness, which is then either cut up into chips in a rotating cutting machine or formed into strands in an extruding machine. When the material is to be used for insulating wires the chips or strands are fed into the wire-coating machines, about which more will be said later; first we have to deal further with the plasticizers.

It has already been intimated that the quality of a PVC product stands or falls with the quality of the plasticizers. These substances are therefore of just as much importance as the polyvinyl chloride itself. They have to answer a number of requirements, some of which are opposed to each other. One of the most important conditions has already been mentioned: a plasticizer must not be volatile, otherwise it would gradually evaporate from the PVC material, which would then become hard and brittle, especially at high temperatures. This has been the experience with certain kinds of PVC products during the war, in which the rather volatile dibutyl phthalate was used as a plasticizer. Nowadays sufficient supplies of plasticizers are available which do not show this fault at all, as for instance tricresyl phosphate.

Apart from evaporation, an inferior plasticizer may leave the PVC material in various other ways and thus equally detract from the durability of such a material. For example, some are subject to decomposition (caused by high temperature or by high relative humidity such as occur in the tropics, and also from the action of ultra-violet rays), or else through migration they may be absorbed in some other plastic or oil with which the PVC may come into contact.

This latter phenomenon is governed by the mobility of the plasticizer and by the extent to which the contacting plastic has an affinity for it. This will be reverted to later.

Stabilizers

Polyvinyl chloride contains more than 50 wt % of chlorine, so that it is not surprising that at high temperatures HCl tends to become separated. This is an autocatalytic process, the HCl formed promoting the separation of still more HCl. It is therefore necessary to counteract this separation right from the beginning, and this can be done by adding a substance (the stabilizer) as for instance lead stearate, which binds HCl in an inactive form. With such a stabilizer the PVC material can withstand temperatures up to 150 °C for a long time without any adverse consequences.

Other substances serve as stabilizers for counteracting the effect of ultra-violet rays. Both the plasticizer and the polyvinyl chloride itself can be made insusceptible to these rays by means of suitable stabilizers. The scope of the present article does not allow us to go further into the mechanism of this process.

Pigments

The fact that PVC materials can be made in all sorts of striking colours and combinations of colours is an important advantage. In the case of multiple-core cables which form the nerves of a telephone exchange, and also for radio and similar apparatus, it is of great value to be able to distinguish readily the various electrical circuits from the colours given to the leads.

At first the pigments employed were those used for colouring rubber, but now preference is given to specially prepared pigments of greater dispersability, which at the same time stand up better against heat and light.

By a certain method of extrusion (the process described below by means of which the PVC material is applied to the wire that is to be insulated) or of finishing, a wire can be marked with a second colour, thereby considerably extending the number of circuits that can be distinguished.

Fillers

The insulating capacity and the resistance to heat of the PVC material are improved by the addition of small quantities of certain kinds of clay. Such fillers also have the advantage of reducing cost owing to their cheapness, but the manufacturer should not be tempted into using excessive amounts because then the final product would suffer considerably in quality. The same is the case when other fillers are used, so this is a point that has to be carefully watched.

Lubricants

The last of the admixtures to be mentioned are the lubricants, which are added so as to facilitate extrusion. Their action is based on the fact that they are not readily miscible with the other ingredients. They form a thin lubricating layer on the outside of the mass and thus prevent direct contact between the mass and the hot metal wall of the extruding machine. Incidentally this layer also reduces the risk of decomposition and discoloration and at the same time gives a higher gloss to the extruded material.

Among the substances used as lubricants are the salts of fatty acids (magnesium stearate, calcium stearate) and, sometimes, also paraffin wax, in quantities of 0.5 to 2%.

Properties of PVC materials

After this brief review of the constituents of PVC mixtures we have to consider the properties of PVC materials and how these are affected by the nature and quantities of the admixtures. Speaking in general terms it may be said that all the admixtures affect the quality of the final product; this applies especially to the plasticizers, in some cases also to the pigments, and even to a certain extent to the agents used in the preparation of the polyvinyl chloride itself (emulsifiers, catalysts, coagulators). On the one hand the multiplicity of the effects of these admixtures is a favourable factor, since it affords the possibility of manufacturing a great variety of products, but on the other hand it is obvious that for the manufacture of a product possessing specific properties a thorough investigation and close control over all stages of the manufacturing process are essential.

We shall classify the properties of PVC materials under the headings of mechanical properties, electrical properties and their resistance to ageing, moisture and various chemicals.

Mechanical properties

When considering those admixtures that affect the mechanical properties of PVC materials we shall confine our attention to that which is of the most importance — as its name implies — viz. the plasticizer.

The general rule is that a viscous plasticizer yields a harder PVC product than a more fluid one used in the same concentration. There are, however, quite a number of exceptions to this rule: sometimes the solvability, i.e. the property of saturating the secondary valencies of the molecules of the polyvinyl chloride, is of more importance than the viscosity of the plasticizer. There are, for instance, viscous, resinous, but highly solvating plasticizers which yield an astonishingly flexible PVC product.

The higher the content of a certain plasticizer, the less is the hardness, the modulus of elasticity, the tensile strength and the rigidity of the product; on the other hand the elongation at break increases. An example of this is given in *fig. 1.*

Elevation of temperature gives greater mobility to the molecules, the material becomes softer, more flexible and less strong, the deformation assuming more and more a plastic character. *Fig. 2* shows how the rigidity [3]) of PVC materials made with different plasticizers is affected by temperature. It is clear that in this respect a plasticizer like dioctyl sebacate is more favourable than, say, tricresyl phosphate.

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[3]) Measured according to the specification D 747-43 T of the American Society for Testing Materials.

The fact that most of the (mechanical) properties of PVC are a function of temperature is due mainly to the viscosity of the mixture being temperature-dependent. Much has already been written about this temperature-dependency [4]. As a general rule it may be said that the more aromatic the character of the plasticizer, the greater is the dependency upon temperature. Examples of more aromatic plasticizers are tricresyl phosphate and dibenzyl phthalate. On the other hand, in the case of esters having long aliphatic chains, like dioctyl sebacinate, trioctyl phosphate and butyl acetyl ricinoleate, the viscosity changes but little with temperature.

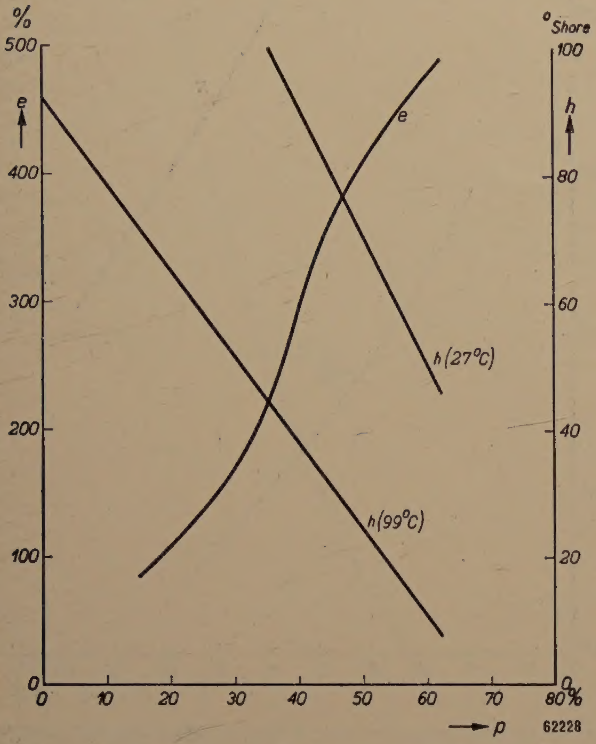

Fig. 1. The breaking strain e and the hardness h, expressed in °Shore, of a certain kind of "Podur", as a function of the plasticizer content p (p in wt % of the quantity of polyvinyl chloride).

Compared with the rubber that is used for insulating, PVC has greater abrasion and tear resistance. It is for this reason that in the U.S.A. for instance rubber has been entirely replaced by PVC for field telephone lines ("assault wire").

Duggan has compared the abrasion resistance of PVC with that of rubber by dragging segments covered with sandpaper over the material under a certain pressure. This test showed that the greater the content of plasticizer the greater is the wearing strength of the PVC product. From Duggan's figures it may be concluded that the kinds of "Podur" used as insulating material have 75 to 100% higher abrasion resistance than a standard rubber mixture answering the specifications D 395-40 of the American Society for Testing Materials.

As far as other properties are concerned good grades of PVC materials are on a par with or closely approximate the best kinds of rubber. From *table I* it appears that most properties are subject to considerable variations, but it should be borne in mind that the values given here cannot be combined arbitrarily; high elongation, for instance, cannot go hand in hand with great hardness.

Table I. Some mechanical properties [5]) of flexible PVC materials.

Tensile strength at normal temp. . .	$10\cdot10^6$-$25\cdot10^6$ N/m² [6]) (100-250 kg/cm²)
Rigidity at normal temp.	$3.5\cdot10^6$-$200\cdot10^6$ N/m² (35-2000 kg/cm²)
Hardness at normal temp.	60-200 °Shore
Elongation at break, at normal temp.	100-500 %
Permanent deformation under a compression load of $7\cdot10^5$ N/m² (7 kg/cm²), at 70 °C	10-15 %

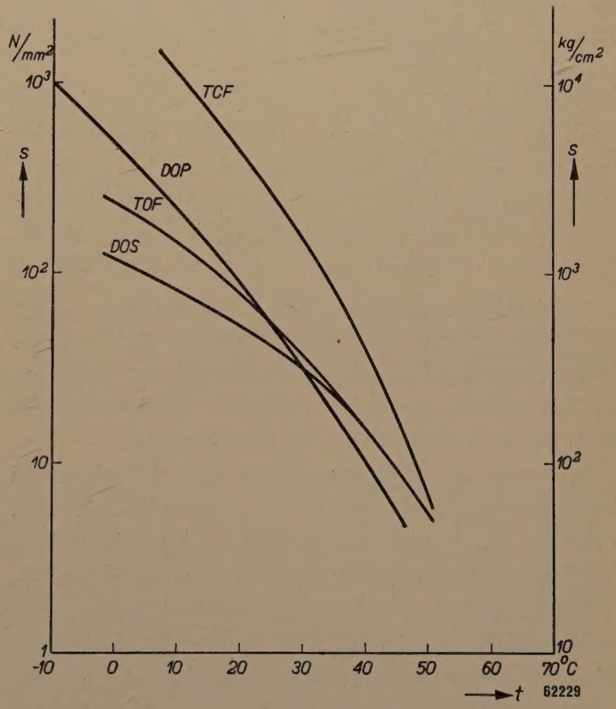

Fig. 2. The modulus of rigidity [3]) s of certain types of "Podur" with different plasticizers (content p = 40% in each case), as function of the temperature t. *TCF* = tricresyl phosphate, *DOP* = dioctyl phthalate, *TOF* = trioctyl phosphate, *DOS* = dioctyl sebacate. For the scale on the left see footnote [6]).

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[4]) See, e.g., H. Jones, Trans. Inst. Rubber Ind. **21**, 298-322, 1946; E. M. Bried, H. F. Kidder, C. M. Murthy and W. A. Zisman, Ind. Eng. Chem. **39**, 484-497, 1947; R. T. Sanderson, Ind. Eng. Chem. **41**, 368-374, 1949 (No. 2).

[5]) Determined according to the specifications of the American Society for Testing Materials.

[6]) 1 N = 1 newton = 10^5 dynes ≈ 0.1 kg force.

Electrical properties

The most important electrical properties are conductivity, dielectric constant, loss angle and breakdown strength.

The conductance of PVC is to be ascribed to the presence of charge carriers, such as ions, which are capable of displacement over relatively large distances. Conductivity increases with the number and mobility of the ions, that is to say, according to the quantity of certain impurities contained in the polyvinyl chloride and in the plasticizer and according to the content of plasticizer and the temperature.

Investigations regarding potentials at the interfaces between inhomogeneous areas in PVC materials have given rise to the question whether a PVC material exposed to direct current does not in course of time change in its properties. Würstlin [7]) found, indeed, that under the influence of a direct voltage applied for a long time a highly diluted solution of polyvinyl chloride in different plasticizers splits up into two layers, one poor and the other rich in plasticizer. But, it should be added, Würstlin used for his tests a polyvinyl chloride that contained impurities, due to the method of manufacture, so that electrically it was less satisfactory.

The kinds of PVC behaving well in this respect, such as "Podur", have such little conductivity that even after ten years no change is to be expected. Following upon the American and German tests already mentioned, we have carried out durability tests with "Podur" wire. Neither under 600 V direct voltage nor under 220 V alternating voltage could any changes in the structure of the insulating material be found even after long exposure, a fact which would be expected considering the high insulation resistance of this material.

Not only the plasticizers but also the pigments influence the resistance of PVC. Some of them may, even in the small concentration of 0.5%, reduce insulation by a factor of 10 or even as much as 100.

Figs. 3 and *4*, relating to a particular case, give an idea of the manner in which the specific resistance of PVC depends upon the temperature and the content of plasticizer. In fig. 3 a curve is added for a good quality rubber, showing a temperature-dependency similar to that of PVC but lying higher. For almost all practical purposes however the insulation resistance of PVC is more than ample.

The dielectric properties of PVC are typically those of a polar plastic. Particularly the polyvinyl chloride molecules contain dipoles in large numbers, viz. bonds of carbon and chlorine atoms. When the PVC is exposed to an electric alternating field then, owing to their limited mobility, the dipoles lag behind the alternations in the direction of the field (after-effect [8])). Corresponding to this lag is a phase shift δ between the field strength and the dielectric displacement, which means that losses occur in the dielectric.

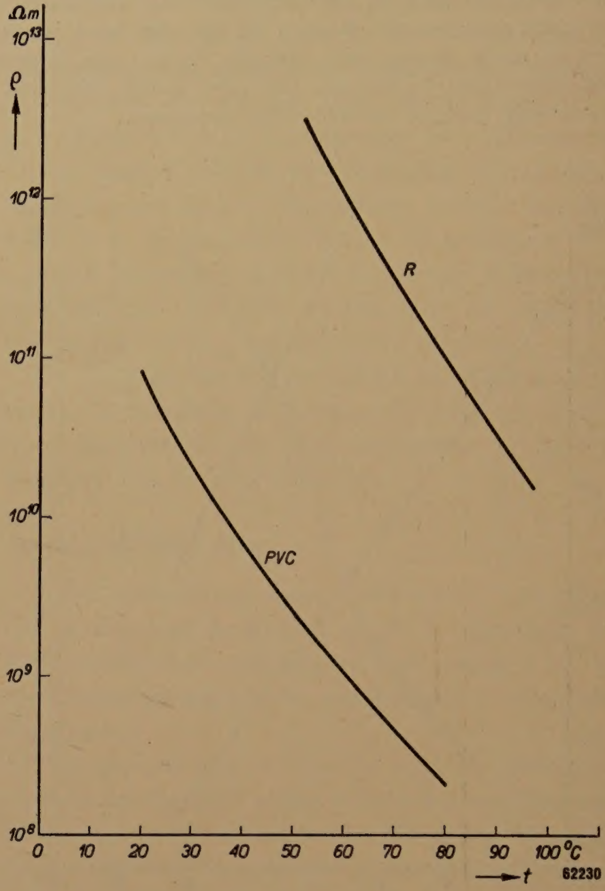

Fig. 3. Specific resistance ρ of a flexible kind of PVC (*PVC*) and of rubber (*R*) of comparable flexibility, as function of the temperature *t*.

In the simple case where there is only one relaxation time τ to be reckoned with, it can be calculated that tan δ as a function of the frequency f of the alternating field has a maximum at $f = 1/(2\pi\tau)$. With most materials, however, there are several relaxation times, differing, moreover, in their dependency upon temperature. Circumstances may be such that at one particular temperature, in a wide frequency band, tan δ changes but little, whereas at other temperatures it shows one or more maximum values. And this is in fact what is observed in the case of PVC materials (*fig. 5*).

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[7]) F. Würstlin, Kunststofftechnik **11**, 269-272, 1941.

[8]) See J. L. Snoek and F. K. du Pré, Several after-effect phenomena and related losses in alternating fields, Philips Techn. Rev. **8**, 57-64, 1946, and M. Stel and E. C. Witsenburg, Heating by high-frequency fields, II. Capacitive heating, Philips Techn. Rev. **11**, 232-240, 1950 (No. 8), in particular under "Nature of the dielectric losses".

The graphs for the dielectric constant show a less freakish picture, falling gradually with increasing frequency and rising gradually as the temperature rises (*fig. 6*).

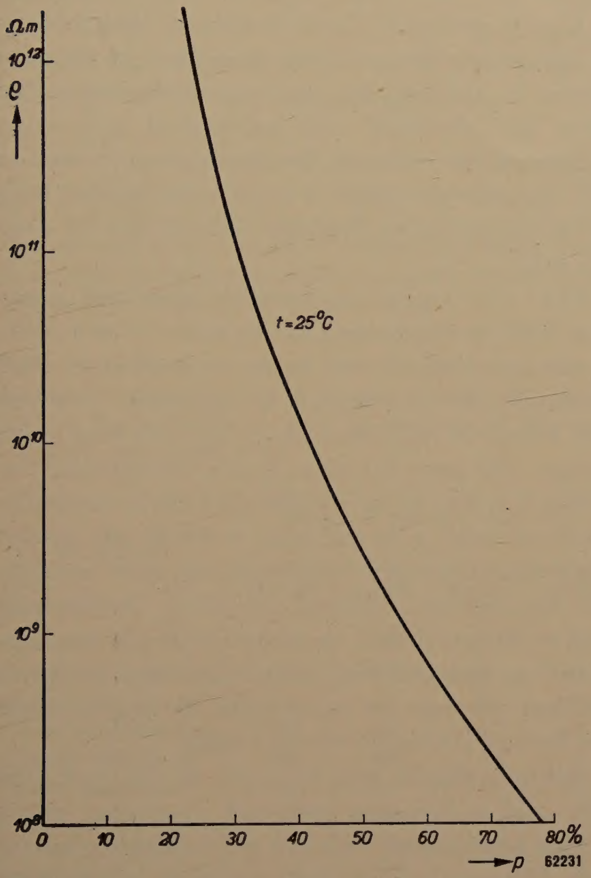

Fig. 4. Specific resistance ϱ of a kind of PVC as function of the plasticizer content p at 25 °C.

From figures 5 and 6 it follows that, generally speaking, PVC is not suitable as an insulating material in tuned circuits: tan δ (in the order of 0.1) and the relative dielectric constant (averaging about 5) are both too high and too temperature-dependent. Very little can be done about this by choosing a different plasticizer, because the dielectric losses are mainly due to the chlorine-carbon dipoles of the polyvinyl chloride itself. These dipoles are far more numerous than those of the plasticizers to be considered, so that it would serve little purpose to use a less polar plasticizer.

The dielectric strength (voltage gradient at which disruption takes place) has been plotted in *fig. 7* as a function of temperature. It is seen that it becomes less with rising temperature and that it is greater for direct voltage than for alternating voltage (even when reckoning with the peak value of the alternating voltage).

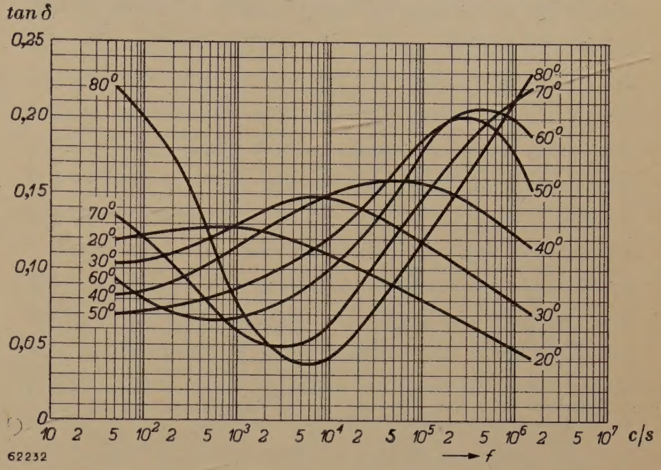

Fig. 5. Loss factor tan δ of "Podur" as function of the frequency f at different temperatures t (20 - 80 °C).

Resistance to ageing, moisture and chemicals

The polyvinyl chloride molecule stands up well against many anorganic acids, alkalies and salt solutions. The molecule is moreover saturated, that is to say it does not contain any double bonds (contrary to rubber for instance). The latter feature is favourable as regards durability but on the other hand it means that polyvinyl chloride cannot be vulcanized in the classical way [9]).

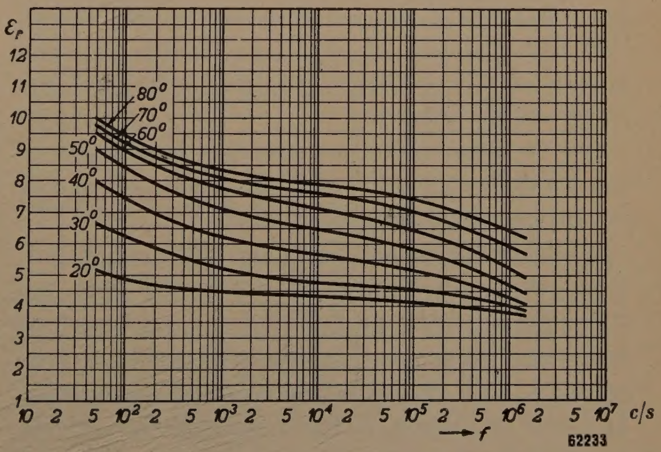

Fig. 6. Relative dielectric constant ε_r of "Podur" as function of the frequency f at different temperatures t (20 - 80 °C).

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[9]) By classical vulcanizing is to be understood the conversion of double bonds into single ones, the free valencies being used for forming cross bridges to neighbouring molecules with the aid of sulphur. Vulcanizing reduces the thermoplasticity of the material.

Greater danger originates from the admixtures. Provided these are well chosen, however, PVC is proof against oxygen and ozone in concentrations which cause rubber to age very quickly. Under the influence of ultra-violet rays there is some danger of decomposition, but, as already stated, this can be counteracted by adding certain stabilizers. The right choice of these substances depends largely on the purity of the plasticizer and the nature of the pigments.

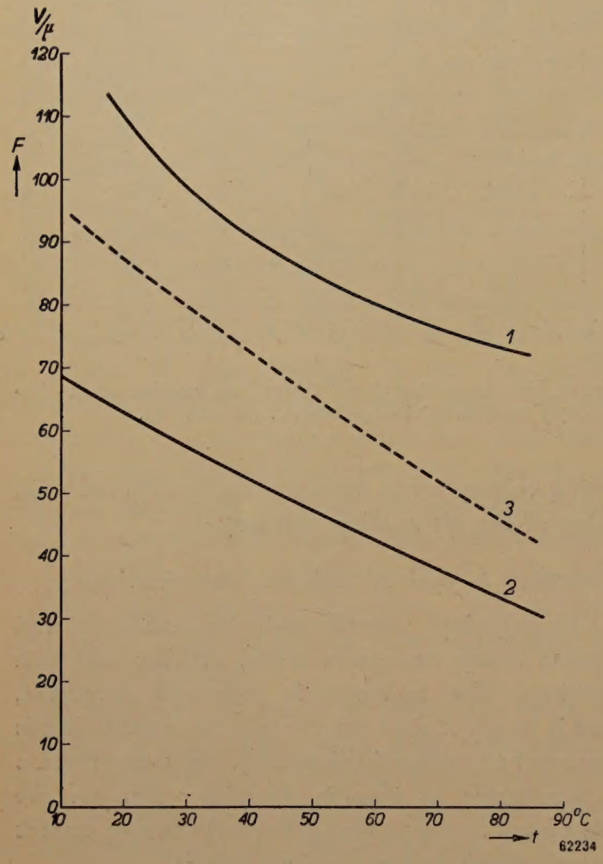

Fig. 7. Voltage gradient F at which breakdown takes place in "Podur", as function of the temperature t. Curve *1* is for a direct voltage, curves *2* and *3* for an alternating voltage of 50 c/s (*2* gives the R.M.S. value, *3* the peak value of F). At each test the gradient was raised to the breakdown value in 20 seconds.

In the introduction mention has been made of the non-inflammability of PVC, a most important advantage compared with rubber.

Most plasticizers are esters and therefore saponifiable (by saponification is understood here the reformation of the alcohol and the acid used to make up the ester). Saponification yields volatile products with unfavourable electrical properties. The rate at which it takes place differs widely as between one plasticizer and another. Tricresyl phosphate for instance saponifies very slowly, but PVC materials made with this plasticizer do not stand up so well against light as those made with phthalates.

Some organic substances cause more or less swelling in PVC materials. After evaporation of the swelling agent the material resumes its original shape and mechanical strength. Use is made of this phenomenon for covering objects with a protective layer: an extruded tube of PVC is caused to swell in acetone, which has a very strong swelling action, and then passed over the object. After the swelling agent has been evaporated the PVC tube shrinks tightly round the object and forms a strong covering layer of good appearance.

A good quality PVC material stands up excellently against moisture. Long immersion in water or burial in the ground has practically no effect upon the electrical and mechanical properties, as proved, for example, by the test mentioned in the introduction where a cable after having been left in the ground twelve years was still in very good condition.

This resistance to moisture does not mean that PVC is impermeable to water. For a cable consisting only of one or more cores and PVC insulation the penetration of moisture — which as a matter of fact takes place only to a very small extent — is quite harmless. It is a different matter, however, with a cable in which the cores are mutually insulated with a hygroscopic material like paper; the usual watertight lead sheathing may certainly not be replaced off-hand by PVC. Incidentally it is to be noted that there are synthetic products based on polyethylene or polyisobutylene which are less pervious to water than PVC, but these are beyond the scope of this article.

Mention should also be made of the fact that PVC and copper do not react upon each other, so that bare copper wire can quite safely be coated with PVC; such is not the case with rubber, since rubber and copper show a strong interaction, which is the reason why they have to be separated, for instance by using tinned copper wire. For the sake of easy soldering, however, tinned copper wire is sometimes used also with PVC insulation, as in the case of "Podur" hook-up wire.

It has already been remarked that when PVC is in contact with certain plastics, migration of the plasticizer is apt to take place. This may be harmful both for the PVC and for the contacting material (which of the two suffers most depends in the first place upon the relative quantities). It occurs particularly when PVC is in contact with polystyrene [10]) and with cellulose nitrate, especially with those kinds of the latter which have a small molecular weight, such as the cellulose nitrate used in the lacquer with which metal lamp fixtures, wooden radio cabinets and suchlike are sprayed. In unfavourable cases it is not long before so much of the plasticizer migrates as to cause the PVC to stick to the lacquer, much to the detriment of its mechanical strength ("lacquer lifting" or "surface marring").

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[10]) Polystyrene is better known under various trade names, such as "Distrene", "Lustrex", "Lustron", "Styron", "Trolitul", etc.

The remedy against this migration is to use plasticizers with heavier and thus less readily displaceable molecules. It has been found, for instance, that polyesters are much less liable to migrate than non-polymerized plasticizers.

Table II gives comparative figures for the migration of different plasticizers into some plastics contacted with PVC. It is seen that an improvement with respect to one plastic does not necessarily mean an improvement for others: trioctyl phosphate, for instance, is very little absorbed by polystyrene but very much more so by cellulose nitrate.

Table II. Comparative figures for the migration of different plasticizers from PVC into various plastics in contact with it. The softeners are listed in the order of decreasing migration into polystyrene.

Plasticizer	Plastic in contact with PVC			
	poly-styrene	cellul. nitrate	cellul. acetate	ethyl cellulose
dibutyl sebacate	170	140	38	55
cresyldiphenylphosph.	168	253	16	41
dioctyl sebacate	163	113	0	21
benzylbutyl phthalate	159	158	18	19
tricresyl phosphate	105	154	3	0
dibutyl phthalate	91	162	74	50
dioctyl phthalate	78	88	70	7
trioctyl phosphate	43	270	18	19
polyester 3	22	76	0	0
polyester 1	14	51	5	0
polyester 2	0	121	1	0

Further it should be noted that there are also certain plastics — polythene is an example — which apparently do not absorb any plasticizer at all from the PVC, at least not in any chemically measurable quantity. And yet a gradual increase of the dielectric losses proves ummistakably that something does nevertheless happen. A typical example of this is found in the case of cables used in the beginning of radar technique. These cables had a polythene dielectric and a protective coating of "ordinary" PVC (with light plasticizers). It was noticed that the losses in these cables were getting greater and greater until ultimately they became prohibitive. This evil was overcome by changing over to cables coated with a PVC material in which exclusively heavy plasticizers were used.

What has been said above about the migration of the plasticizer into plastics applies in the main also for migration into oil. Oil does not react upon or dissolve the polyvinyl chloride itself, but in course of time it extracts the plasticizers. Again with oil, a great improvement is obtained when heavy plasticizers are used, such as polyesters, synthetic rubbers, etc.

Finally, a few words about the tropic-proof qualities of PVC materials. From their behaviour with respect to moisture, elevated temperature, and ultra-violet rays, it can be concluded that the better kinds of PVC may indeed be said to be tropic-proof. When the thermoplastic properties are not overlooked and no cotton or rayon is used for the insulation — these textiles deteriorate rapidly in the tropics — the use of PVC results in an enormous advance compared with rubber, as proved by the experience gained with "Podur" in Indonesia.

By way of illustrating the fact that the weak points of PVC are by far outweighed by its strong points, the case may be mentioned of an American factory where highly aggressive substances are used, such as caustic soda, hydrochloric acid, chlorine and sulphuric acid. Sometimes also very high or very low temperatures prevail in this factory, together with a high degree of humidity, factors which can certainly not be considered as favourable for the durability of an electrical installation. The cables in this factory are laid in channels in the concrete floors. They are mostly insulated with PVC, but, owing to this material being rather scarce at the time, some of the cables were insulated with rubber. Within a year the rubber cables started to cause trouble, so much so in fact that they had to be replaced. But the PVC cables have shown no defects whatever even after three years.

Coating wire with PVC

It has already been described how PVC is obtained in the form of chips or strands for feeding into the wire-coating machines. These machines, like those which produce the strands, are based on the principle of extrusion. A cross-sectional diagram of such a wire-coating machine is given in *fig. 8.* A worm rotating in a heated cylinder conveys the PVC from the feeder to the crosshead.

On its way the material is gradually heated, so that upon reaching the crosshead it is in a plastic state. Inside the crosshead it passes round a hollow pin called the mandrel or torpedo, through which the wire to be coated (bare or tinned copper wire) is drawn. The point of the mandrel reaches just into the die or outlet of the crosshead, where the coating takes place. By means of set screws the mandrel can be placed exactly concentric with respect to the die, so as to ensure that the insulating layer is of the same thickness all round. *Fig. 9* is a photograph of one of these machines.

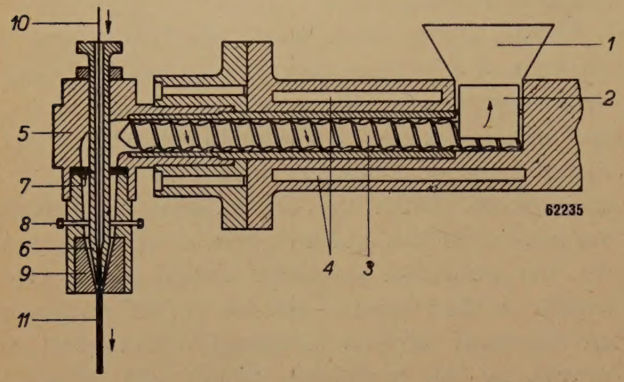

Fig. 8. Sectional diagram of a wire-coating machine. *1* filler, *2* drum carrying the chips of PVC to the conveyor worm *3*, *4* channels containing heating elements, *5* crosshead (with mandrel *6*, filter plate *7*, centering pins *8* and die *9*). *10* bare wire, *11* insulated conductor.

Careful attention has to be paid to the temperature variation of the PVC in this machine. If temperature is too low the surface of the insulated wire is rough and the material no longer passes the heat shock test described below. If the temperature is too high then again the wire is not of good appearance and, moreover, there is a risk of decomposition. Decomposition also arises in dead corners where the material is exposed to a rather high temperature for some length of time, so that it is of great importance that there should be no such dead corners where the PVC can stagnate.

The coated wire has to be tested for eccentricity. For those kinds of wire where a slight eccentricity does no harm it is specified that the breakdown strength must nowhere drop below a certain limit. In the testing machine the wire is passed at a high speed through a salt solution, with a high potential difference (say 6000 V) between the bath and the core. As soon as a breakdown takes place the testing machine is automatically stopped, this being done so quickly that the defective spot on the wire can easily be traced before having reached the take-up reel.

Wire intended for telephone cables needs a sharper test. The slightest eccentricity causes capacitive asymmetries in the cable, which result in cross talk. For the testing of these wires an apparatus has been devised through which the wire is passed as it comes straight from the coating machine and in which the slightest eccentricity is immediately detected, this then being corrected at once by means of the mandrel-adjusting screws, without having to stop the coating machine. This is a great advantage, because the manufacture can continue without interruption. When the machine had to be stopped, as was the case with the testing method formerly applied, there was a danger of decomposition of the PVC owing to its being left too long in the machine at a high temperature; once that process had begun it tended to spread through the mix, thus very soon making it necessary to give the whole of the machine a thorough clean-out.

Tests to which the coated wire is further subjected will be dealt with in the next section of this article.

When no bare wire is fed through the crosshead and the mandrel is advanced so as to protrude a little beyond the die then, as is quite obvious, the machine produces PVC tubing. Sleeving for mounting purposes is made in this way.

Types of "Podur" products

Without any attempt at giving such complete details as may be found in a catalogue, a description is given of the most important "Podur" products, with their fields of application and the main requirements that have to be satisfied in each particular case.

Connecting wire and flex

In its simplest form "Podur" connecting wire (including hook-up and applicance wire) consists of tinned copper wire with a single insulating layer of PVC. A coating 0.4 to 0.6 mm thick suffices in order to meet all the requirements specified by Philips Material Testing Department for wire carrying voltages up to 1000 V A.C. or 1500 V D.C. It would lead us too far afield to go into all these requirements, but two of them may well be mentioned here:

1. After 24 hours immersion in water at 20 °C
   a) the breakdown voltage, measured in mercury, must be higher than 7000 V A.C. (R.M.S. value) (actually it lies around 20,000 V), and
   b) the insulation resistance of 1 metre of wire

at 20 °C must exceed 100 megohms and 1 megohm at 70 °C.

2. After two hours in an oven at 140 °C the insulation must not show any cracks and the breakdown voltage at 20 °C must be higher than 7000 V A.C.

This second requirement might lead to the wrong conclusion that this wire can be used also at a temperature of 140 °C. Although the properties of PVC are unchanged after it has cooled down again to room temperature, a high working temperature is not permissible because then the PVC gets soft and it needs but little force to remove it from the wire. The heat-shock test specified is intended only as a test for the extrusion; if the extrusion is not carried out under exactly the correct conditions stresses arise in the PVC and when the heat-shock test is applied these stresses cause cracking.

The connecting wire is intended for fixed electrical connections inside electrical apparatus. If there is a possibility of the wire having to be mounted at a low ambient temperature it is not wise to use the hardest kind of "Podur", because in time the insulation is apt to break as a result of the repeated bending to and fro. The lowest temperature at which the wire can be used without this risk arising depends not only upon the kind of "Podur" but also upon the core diameter *d*. In order to investigate this question we constructed a simple device with which bending tests can be carried out in a reproducible manner and at different temperatures. These tests show that if it is required that the insulation should not break before the copper core itself, wire with $d \geq 1.0$ mm and insulated with hard "Podur" may only be used for mounting at temperatures above 10 °C, and that wire with $d \leq 1.8$ mm and insulated with moderately soft "Podur" can still be used below a temperature of 0 °C.

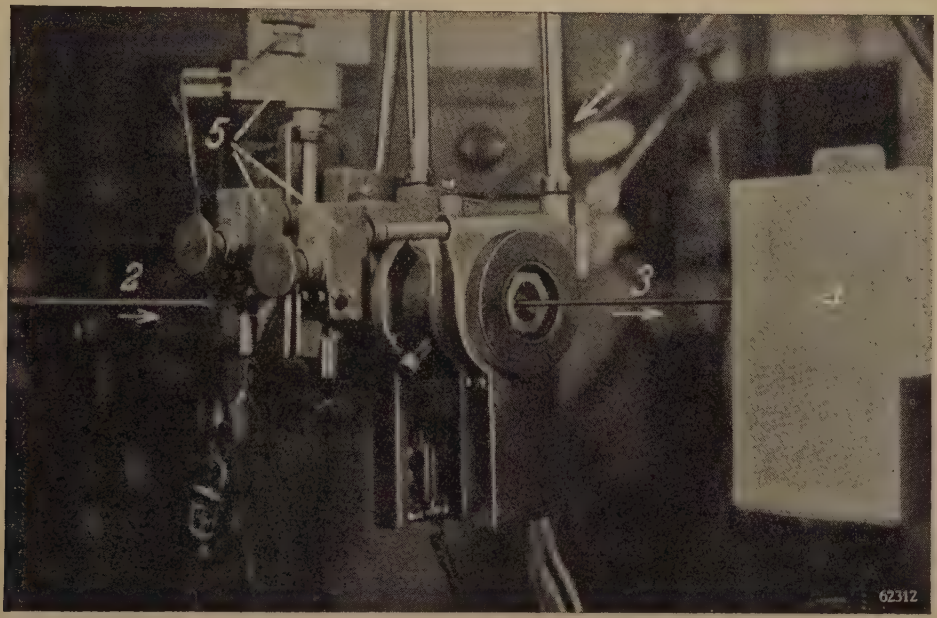

Fig. 9. Photograph of a wire-coating machine fed with a strand of PVC (*1*) instead of chips. *2* the bare wire, *3* the PVC-insulated wire, which is cooled in *4*. *5* are the temperature control instruments.

Where a flexible connection is required in an apparatus preference should be given to mounting flex with a stranded core consisting of a number of soft, tinned copper wires. One example of the use of such a flex which might be mentioned here is the illumination of Christmas trees, for which purpose the PVC-insulated flex is ideal, because it is non-inflammable, is more durable than rubber (so that it can be used for a great many years), is quite safe as regards dielectric strength (breakdown voltage >1000 V A.C.) and can be made in a suitable colour; usually it is green, but sometimes preference is given to transparent PVC flexes.

In addition to the single-core flex, flexes are also made with two insulated cores twisted together. Both the single- and the twin-core flex can be screened with a copper wire braiding, with or without an outer sheathing of flexible "Podur". These constructions, however, are not suitable for high frequencies.

Connecting wire is also made with "Podur" insulation thicker than 0.5 mm, say with a thickness of 1.6 mm, which is suitable for working voltages up to 6000 V A.C. or 10,000 V D.C.

With all these kinds of mounting wire and flex, if there is any chance of a high temperature being reached, care must be taken to avoid the possibility of any force being brought to bear upon the wire as this would be likely to push the insulation away.

Insulating sleeving

"Podur" sleeving answers the American specifications (American Society for Testing Materials, D 876 and D 922) as regards insulation resistance, dielectric strength, breaking stress, tensile strength, resistance against oil and ageing, while it also just answers the "penetration" test, which requires that the thermoplasticity must not be so great that above a certain temperature and at a given pressure the core would be exposed.

In cases where it is difficult to avoid conditions whereby the insulating material might be pushed away it is often possible to make allowance for this by using a thicker coating or a harder kind of PVC.

"*Parallel connecting flex*"

For the connecting leads of radio sets, reading lamps, etc. flexes are made with two parallel cores (not intertwisted). This parallel-core connecting flex is available in various colours, offering a choice of shades matching any surroundings.

A special type of this kind of flex has been made for the "Philishave" dry-shaver (*fig. 10*), which has to be very flexible to stand up against the daily rolling up and unrolling, whilst moreover, since it is frequently in contact with the hands, the insulation has to answer very high requirements. It is required, for instance, that after 48 hours in an atmosphere of 94% relative humidity the insulation resistance of 1 metre of each core at 20 °C has to be greater than 100 megohms, and after 48 hours immersion in water the breakdown voltage between cores has to be higher than 5000 V A.C. (the permissible working voltage is 500 V A.C. or 750 V D.C.). The measured insulation resistance of 1 metre is about 2000 megohms. The condition specified in Switzerland, that the leakage current of 2 metres of cable in water of 50 °C to which an A.C. voltage of 500 V is applied must be less than 0.5 mA, is amply satisfied. (This requirement was based on the consideration that a current of 5 mA passing through the human body may cause such cramp as to make it impossible to release the grip on the cable, and that the first symptoms of shock occur at a current of 1.7 mA peak value.)

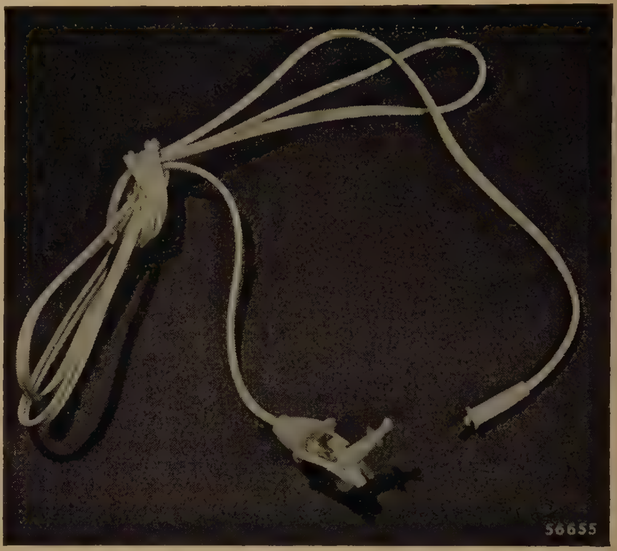

Fig. 10. "Podur"-insulated flex for the "Philishave" dry-shaver.

Flex (or cable) with two or more intertwisted cores

Flexes or cables with 2, 3, 4, 7, 12 or 19 intertwisted cores, with core diameters varying between 0.75 and 6 mm², are manufactured for all sorts of purposes.

Not only the cable as a whole but also each individual core has to satisfy certain demands as regards insulation resistance, breakdown voltage and loss angle. With separately tested and approved cores it has been possible to build up highly dependable cables, only the cores themselves having to be rejected where necessary.

If necessary these cables can be supplied with a shielding and a PVC outer sheath.

High-tension cable for television tubes

A thin cable was required for a television receiver [11]), for connecting the cathode ray tube to the supply unit delivering an anode voltage of 25 kV. It was specified that this cable had to withstand a D.C. voltage of 40 kV for two minutes at 65 °C and that a length of 1 metre should show an insulation resistance of more than 1000 megohms. The insulating material has to be resistant to oil (the parts of the supply unit are contained in a can filled with oil) and it has to make a seal tight enough to prevent oil leaking out between the core and the insulation. These requirements have been met by making a cable (*fig. 11*) with a thick coating of "Podur" of a kind specially prepared for the purpose (outer diameter 4.4 to 4.7 mm). The ingredients for the mixture and the manner of processing have to be carefully tested.

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[11]) G. J. Siezen and F. Kerkhof, Projection-television receiver, III. The 25 kV anode voltage supply unit, Philips Techn. Rev. **10**, 125-134, 1948.

Telephone cable

Telephone cables (not intended to be laid underground) are being made with 3 to 37 groups of cores, each group consisting of two, three or four conductors. Each core is insulated with "Podur" in different colours (red, blue, yellow, green, black and white) according to a specified colour scheme. The intertwisted cores are sheathed with grey "Podur".

Since it would be impracticable to give such large numbers of cores each a different colour, two or more colours are used per core. The additional colours are printed on in the form of helical lines round the core, for which a special machine has been designed.

Mention has already been made of the precision with which the core is centered in the insulation in the manufacture of the coated wires. The slightest eccentricity gives rise to cross talk. The finished cable is likewise tested for such tendency (*fig. 12*).

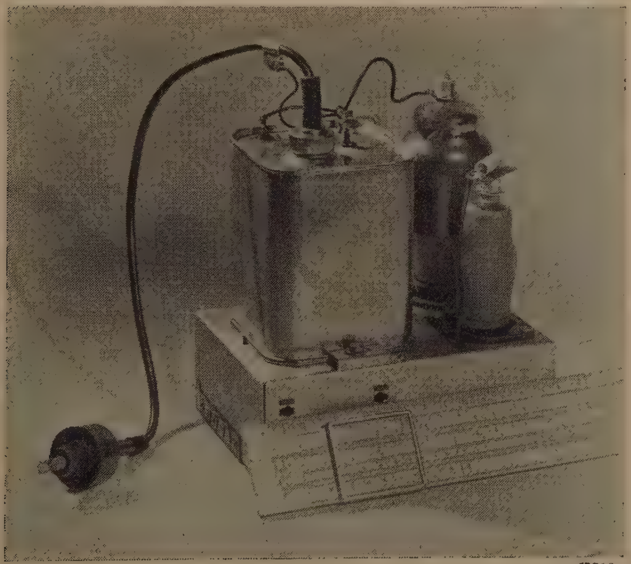

Fig. 11. Anode supply unit for supplying 25 kV anode voltage to the cathode ray tube of a television receiver. On the left the "Podur"-insulated cable connecting up to the cathode ray tube.

As regards the other inspection tests, briefly these amount to an insulation resistance for 1 metre of cable exceeding 10^4 megohms and a capacitance less than 100 pF/m at 25 °C between the two wires of each pair.

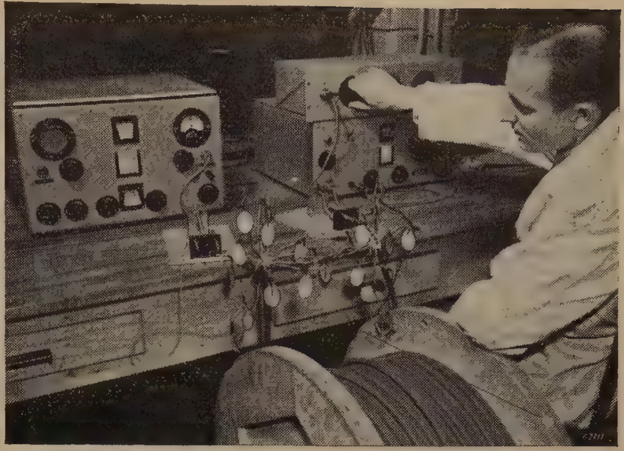

Fig. 12. Measuring the cross-talk damping between the pairs of conductors in a telephone cable. A certain voltage supplied by the generator (left) is applied to one pair of conductors. The resulting voltage on other pairs is measured (right) and must not exceed a certain value. Measurements are taken at different frequencies (100 to 500 kc/s).

Microphone flex for telephones

The flex used for connecting the microphone to the other parts of a telephone has to be particularly flexible and must withstand bending a large number of times.

With a view to obtaining the desired flexibility, so-called tinsel is used (a thin strip of copper wound round a thread of artificial silk), and for the insulation of the wires an exceptionally flexible kind of PVC (red and blue, yellow and green for the different cores, which are four, three or two in number). Notwithstanding its great flexibility, the insulation resistance of this cable, per metre, still exceeds 100 megohms as tested at 20 °C and after 6 hours at 90% humidity.

The cores are intertwisted and braided with cord. The breakdown voltage between the cores has to be higher than 1000 V, and after the flex has been bent to and fro 6000 times there must not be any "crackling".

Microphone flex for amplifiers

"Podur" microphone flex has two or four conductors, which, since resistance is of no importance, may be thin (0.3 mm in diameter; they are made of cadmium-copper for strength). The cores are separately insulated with PVC, intertwisted, screened and once more insulated with a sheathing of PVC. This cable is tested for insulation resistance, screening of the cores and microphony (the occurrence of potential differences in the cable due to bending or twisting).

Flex for hearing aids

Modern hearing aids consist of a small box containing a microphone, amplifier, and batteries and a miniature telephone worn in the ear. They are usually required to be as inconspicuous as possible.

The flex connecting the telephone to the amplifier has been made inconspicuous by using a very thin coating of a colourless, transparent PVC, with an outer diameter of no more than 1.6 to 1.7 mm. It has two very flexible conductors ("tinsel"). Owing to the small dimensions — calling for the utmost precision in manufacture — and the high flexibility of the PVC, a very flexible lead has been obtained which causes no inconvenience whatever to the wearer of the hearing aid.

This summary must suffice for the present. It is hoped that it has sufficiently proved that PVC insulating material has already acquired a position in many fields.

Summary. Following upon a discussion of the components used for preparing wire-insulating materials based on the synthetic resin polyvinyl chloride, some of the properties of these materials are dealt with under the headings of mechanical properties, electrical properties and resistance to moisture, chemicals, etc. Some of these properties are superior to those of rubber (i.e. non-inflammability, abrasion resistance, resistance to chemicals and ultra-violet rays), while others closely approximate them (insulation resistance). Attention is drawn to certain points that have to be watched when using insulating materials, such as thermo-plasticity. An account is given of the extrusion process, by means of which wire is coated with polyvinyl chloride insulation. In conclusion a brief description is given of the principal types of wires with polyvinyl chloride insulation ("Podur") marketed by Pope's Wire and Lamp Works at Venlo (Holland): connecting wire and flex, various special flexes, high-tension cable, telephone table, microphone flex, etc.

INACTIVATION OF BACTERIA BY ULTRA-VIOLET RADIATION

by J. VOOGD and J. DAAMS.

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Radiation from the sun has different effects upon living organisms. It has been found, for instance, that ultra-violet rays of a certain wavelength present in the radiation from the sun stop the multiplication of bacteria and other micro-organisms. Good use can be made of this, without having to depend upon sunlight, by employing a low-pressure, mercury-vapour lamp emitting rays which have a specifically disinfecting power exceeding by far that of sunlight. This lamp presents good possibilities for the solution of some problems of hygiene and for the sterilisation in processing foodstuffs and medicaments.

The fact that millions of pounds worth of foodstuffs are spoiled every year through bacterial action shows how important it is that the growth of these micro-organisms should be checked also in this field.

The influence of sunlight upon bacteria

In the year 1877 the Englishmen Downes and Blount made a discovery of great value for the existence of the human race. They found that micro-organisms cease to multiply when exposed to radiation from the sun for a sufficient length of time. The effect of such exposure can be demonstrated by a simple experiment, the result of which is represented in *fig. 1*, where we see a so-called Petri dish, such as is commonly used by bacteriologists. First a culture medium particularly suitable for making the growth of Bacterium coli visible was placed in this dish. Where the bacteria colonise this culture medium assumes a deep red colour owing to the formation of fuchsin, but where there is no growth of the bacteria it remains clear. A suspension of coli bacteria was seeded all over the surface of the medium in this circular dish. The left half was then exposed for one hour to direct sunlight falling upon it at an angle from the left, whilst the right half was covered with a screen intercepting the ultra-violet rays. After 24 hours' heating at 37 °C the dish showed the picture of fig. 1. The dark part of the medium in the right half indicates mass growth and colonisation of the bacteria. The light half on the left shows that there has been no growth of the bacteria there. The sharp demarcation between the two parts clearly demonstrates the effect of sunlight.

It is to be noticed that the light part does not extend right up to the edge of the dish. On the extreme left a number of strongly developed colonies are clearly perceptible, this being due to the shadow cast by the glass rim of the dish. This shadow effect is interesting, in that it indicates the answer to the question as to what part of the spectrum is most responsible for the inactivating action of the radiation from the sun. The fact is that ordinary glass fully absorbs all rays of a wavelength smaller than 3200 Å, so that — excluding the possibility of specific biological actions of the infra-red rays with wavelengths greater than 30,000 Å, which are likewise absorbed by the glass — the shadow effect of ordinary glass points to the conclusion that the inactivating action is to be ascribed to the small quantity of ultra-violet rays of wavelengths shorter than 3200 Å present in sunlight.

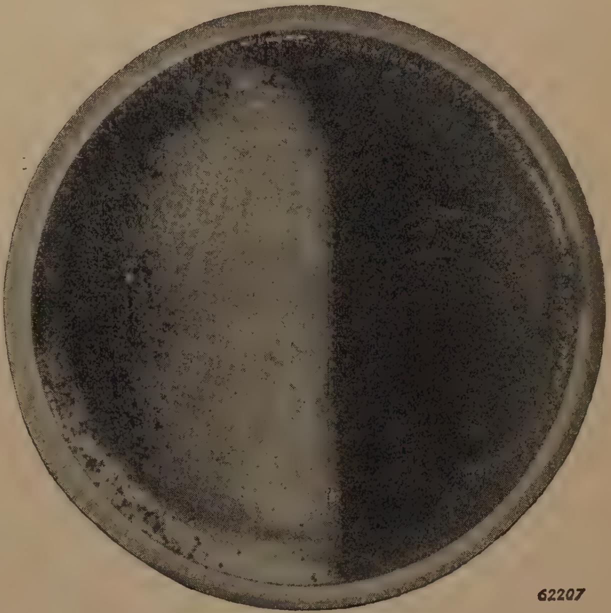

Fig. 1. Development of Bacterium coli. The left half of the dish has been irradiated with sunlight falling upon it at an angle from the left. Owing to the formation of fuchsin the culture medium where colonies have developed is of a darker colour.

The first question to be put is whether these rays act upon the bacteria or upon the culture medium, or upon both. The answer to this is given by an experiment the result of which is to be seen in *fig. 2*. A circular part of a culture medium sown with bacteria was intensely irradiated, after which a piece in the middle of that part was re-sown. After heating it appeared that the non-irradiated bacteria in the middle of the irradiated circle are still able to develop on the previously irradiated culture medium. It is, therefore, to be concluded that the ultra-violet rays in sunlight have the power to stop multiplication of the coli bacteria. Briefly, though not absolutely correct, one speaks of the bactericidal action of sunlight. Analogous phenomena are observed when moulds, yeasts and viruses are irradiated, and consequently one speaks in more general terms of the germicidal action of ultra-violet rays.

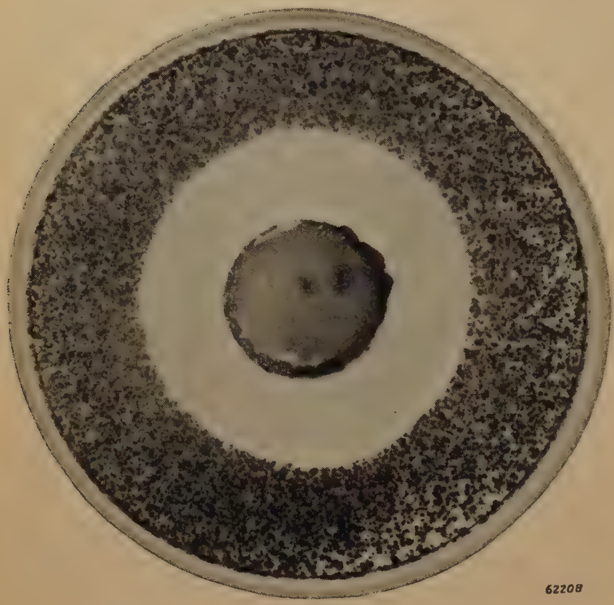

Fig. 2. Development of colonies of Bacterium coli on non-irradiated (outer ring) and irradiated (inner circle) culture medium, showing that the radiation has no effect upon the culture medium.

Spectrum of the bactericidal effect

This discovery of the bactericidal effect of ultra-violet rays very soon led to an investigation into the question of its dependency upon the wavelength of the irradiation, a qualitative answer to which is given in *fig. 3*, which was produced in the following way.

A spectrum of the radiation from an electric discharge in mercury vapour under high pressure was projected, with the aid of a large quartz spectograph with wide aperture, upon the surface of a culture medium sown with a suspension of bacteria. For the radiation a "Biosol" lamp, type B, was used. After incubation the culture medium showed the picture given in fig. 3. Where the projected wide spectral lines are to be seen there was no growth of the bacteria, due to the action of the ultra-violet rays, such in contrast with the immediate surroundings where no or very little ultra-violet radiation reached the culture medium. Below this microbiologically recorded spectrum a photographically recorded spectrum of the lamp used has been reproduced, and below that the spectrum of the germicidal lamp which will presently be discussed.

In this experiment the strong spectral line of 3130 Å shows no bactericidal action, whereas such is the case with the spectral lines of smaller wavelengths.

Of course this experiment gives only a qualitative picture, from which no quantitative conclusions can be drawn regarding the dependency of the bactericidal action upon the wavelength of the radiation. To this end several investigators have taken careful measurements. *Fig. 4* gives curves plotted from information contained in literature on the subject.

Curve (*a*) shows a maximum at 2650 Å and applies with fairly great accuracy both for bacteria and for moulds. Attempts have been made to relate this spectral curve to an absorption process, and absorption curves have been sought which correspond to the bactericidal curve. It is remarkable that the spectral absorption curves of proteins, with a maximum at about 2800 Å, show no correspondence. Better agreement is found with the

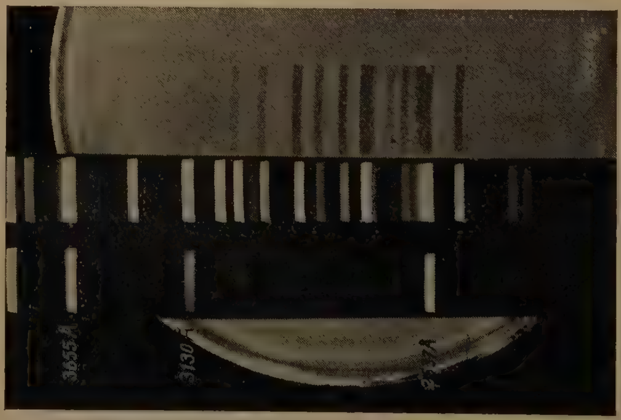

Fig. 3. Biologically recorded spectrum of the bactericidal effect of a "Biosol" lamp type B (*top*). Owing to the recording technique the lines where no bacteria have developed are darker. For comparison, the photographically recorded spectra of a "Biosol" lamp type B (*middle*) and a germicidal lamp, TUV 25 W (*bottom*).

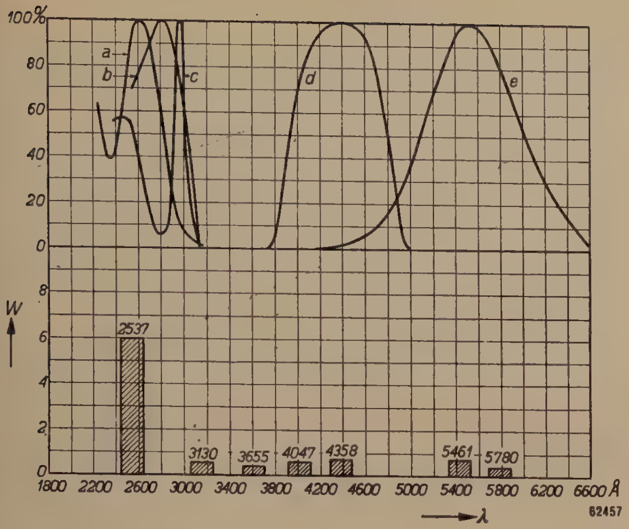

Fig. 4. *Top*: various effects of radiation as function of the wavelength.

- *a*) Bactericidal action (B. coli).
- *b*) Killing effect upon a protozoan (Paramecium multimicronucleata).
- *c*) Erythemal effect.
- *d*) Photographic effect (non-colour-sensitive film).
- *e*) Normal eye-sensitivity.

Bottom: radiation from the TUV 25 W lamp.

spectral absorption of nucleoproteids (substances related to proteins from which, i.a., chromosomes are built up). This is demonstrated in *fig.* 5, where the spectral absorption curve of thymonucleic acid is given as an example of a nucleoproteid.

As regards the mechanism of the inactivation it can be proved that the metabolism in inactivated bacteria partly continues, but without leading to the normal division of cells.

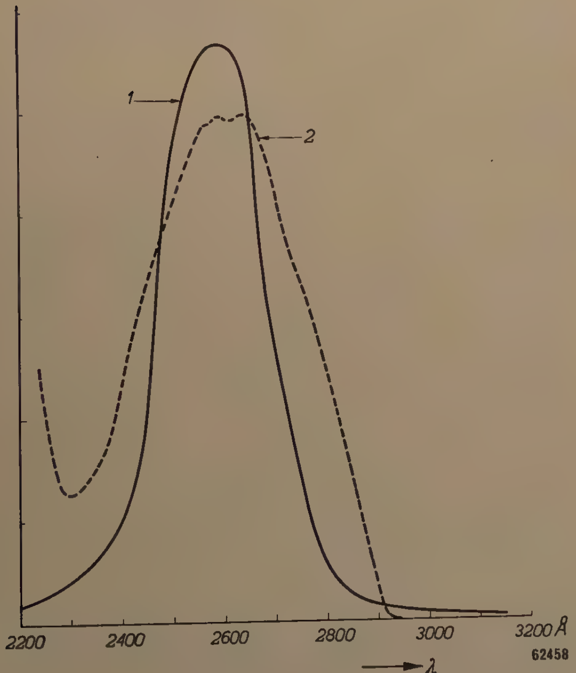

Fig. 5. Bactericidal action as function of the wavelength (*1*) and absorption curve of thymonucleinic acid (*2*).

In view of these phenomena the bactericidal effect of ultra-violet radiation is interpreted as an absorption process in those nucleoproteids performing a fundamental function in the multiplication of bacteria. Apparently this absorption process in itself is not deadly, the result of the irradiation being a normal dying off of the bacteria before multiplication has taken place (bacteriostasis).

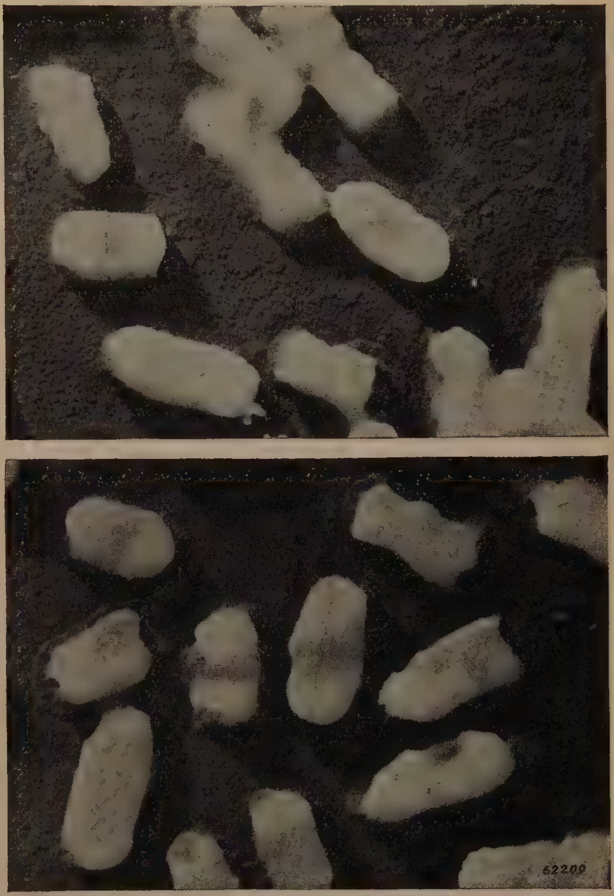

Fig. 6. Photographs taken with an electron microscope showing coli bacteria (enlarged 18,000 times). *Top*: not irradiated, *bottom*: irradiated with ultra-violet. Outwardly there is no difference to be seen.

From photographs obtained with the electron microscope it appears that when irradiating with a dose that undoubtedly stops multiplication of cells there is no outwardly perceptible damage to the bacteria, such as is the case in the destruction of protozoa (e.g. Paramecia) by ultra-violet irradiation. *Figures* 6 and 7 give a good picture of this [1]).

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[1]) It has also been found possible to restore inactivated bacteria to their normal state of multiplying — be it only in part — by powerful irradiation with visible light a short time after inactivation with ultra-violet radiation.

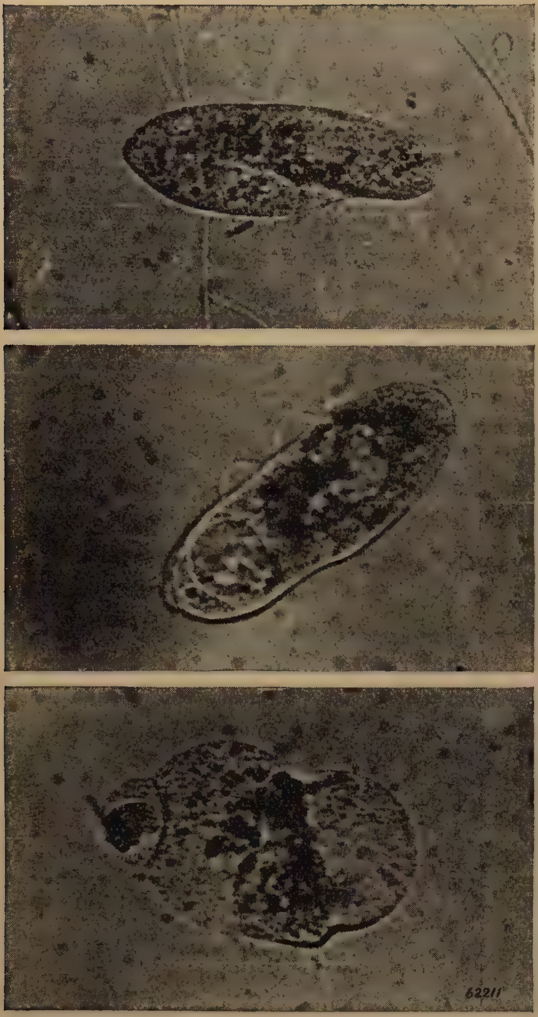

Fig. 7. Photographs taken with a normal microscope showing paramecia (enlargement 250 times). *Top:* not irradiated, *bottom:* irradiated with ultra-violet, in different stages of destruction. Note the blisters formed.

Construction of germicidal discharge lamps

With the modern technique in the manufacture of electrical discharge lamps it is possible to make a special lamp for the action described above, so that one is no longer dependent upon the sun for it.

As we have seen, radiation of a wavelength between 2500 and 2600 Å has a strong germicidal action. A powerful source of radiation within this wavelength range can be obtained by employing the electrical discharge in mercury vapour of low pressure, whereby mainly two resonance lines of the mercury atom are radiated, namely a weak one at 1850 Å and a strong one at 2537 Å.

A germicidal lamp can be dimensioned exactly like the tubular fluorescent lamp for lighting, in which ultra-violet radiation is used for producing visible fluorescent radiation in a powder with which the glass tube is lined.

For the germicidal lamp it is the ultra-violet radiation of 2537 Å that we want to use, that of 1850 Å being undesired on account of its strong ozonising action. Therefore in the manufacture of germicidal lamps the fluorescent powder has to be omitted and the tube has to be made of a kind of glass that passes the mercury line of 2537 Å but absorbs the lines of smaller wavelengths, and especially the resonance line of 1850 Å.

In this way a lamp has been constructed (the TUV 25 W) of which the spectral distribution of the radiation intensity is represented in fig. 4. Since this lamp, as regards the electrotechnical part, is exactly similar to the TL 25 W lamp, the same starter and ballast can be used for both.

The energy of the radiation in the wavelength of 2537 Å is 6 W, but this high output is only obtained when the vapour pressure of the mercury in the tube is of the right value, so that it is greatly dependent upon temperature. In view of the radiation of heat the tube has been so dimensioned that under normal conditions the wall temperature is about 40 °C, which is just right for the most favourable vapour pressure. When under different circumstances, e.g. when the lamp is mounted in a refrigerator the wall of the tube assumes a different temperature, the output is considerably reduced: in the case of deviations of 20 °C the output is about 25% lower.

Radiation doses required

For combating germs with the aid of germicidal lamps the first question to be decided is what power has to be installed.

Although there are a number of complicating factors to be reckoned with it may be taken as a basis that the degree of inactivation depends upon the product of the intensity and the duration of the irradiation.

The various species of bacteria, however, are not all equally sensitive to ultra-violet radiation, as may be seen from *table I*.

A very resistant bacterium for instance is Sarcina lutea, which is about seven times more resistant than Bacterium coli. Moulds are still less sensitive. *Fig. 8* shows how, in the case of a mixture of bacteria and moulds forming, when not irradiated, visible colonies on the culture medium, after irradiation with a suitably chosen dose the bacteria are rendered inactive while the moulds continue to multiply. It is to be taken that in practice for moulds a dose is required 20 to 100 times stronger than that needed for Bacterium coli.

Table I. Doses in mWsec/cm² required for inactivation of 90% of the following organisms (from various publications).

Organism	Dose	Organism	Dose
Bac. anthracis	4.52	Serratia marcescens	2.4
B. megatherium (veg)	1.13	ditto	2.2
B. megatherium (spores)	2.73	ditto	8.3
B. paratyphosus	3.20	Shigella paradysenteriae	1.68
B. subtilis	7.1	Spirillum rubrum	4.4
ditto	6.0	Staphylococcus albus	1.84
B. subtilis (spores)	12.0	ditto	3.30
Corynebacterium diphteriae	3.37	Staphylococcus aureus	2.18
		ditto	2.60
Escherichia coli	3.0	ditto	4.95
Proteus vulgaris	2.64	Streptococcus viridans	2.0
Sarcina lutea	19.7		

From table I it is seen that the values given by various investigators are widely divergent. This is due to the difficulties encountered in trying to obtain quantitative data on this subject. Even when attention is confined to one strain of a certain species of bacteria its sensitivity is found to vary according to the life phase in which the bacteria happen to be at the time of irradiation and also according to the nature of their surroundings.

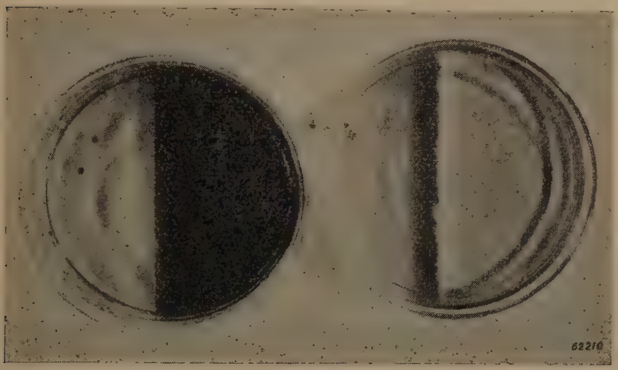

Fig. 8. Cultures on the left half irradiated with a TUV lamp of 25 W at 25 cm distance. On the left coli bacteria irradiated for 2 minutes, on the right a mould (Penicillium spores) irradiated for 15 minutes.

Life phases of bacteria

As is the case with all living organisms, the vital process of bacteria is closely inter-related with the surroundings. This is clearly seen when a small quantity of an old suspension of bacteria is placed in a liquid culture medium, such as sterile broth. In such an old suspension the process of cell division is highly stagnated, due to the influence of the accumulation of metabolic products which inhibit growth of the bacteria in those surroundings. When these bacteria are placed in a fresh medium it takes some time for them to adapt themselves. In this adaptation phase the metabolic processes increase, the volume of the bacteria becomes greater and, as appears from excellent investigations of the Caspersson school [2]), also the content of nucleoproteids increases. As a result of these physiological activities the process of cell division starts anew. The culture then reaches what is called the logarithmic phase, where the number of bacteria increases almost exponentially with time; this phase brings about its own end by the inhibiting action of accumulated metabolic products in the suspension. In the bacteria changes take place which cause the process of cell-dividing to come to a standstill and consequently the natural dying off becomes a factor of importance. Via a stationary phase the culture then reaches the dying-off phase, where the number of bacteria decreases and ultimately the culture dies out.

The various conditions in which the bacteria are found in the ageing of the culture described above are found again in the process of inactivation by ultra-violet irradiation. This can be explained with the aid of *fig. 9*, relating to the following experiment.

A small quantity of a suspension of Bacterium coli in the dying-off phase was placed in sterile broth. The curve on the extreme left of fig. 9 represents the inactivation of this culture in the adaptation phase as a function of the dose of irradiation of 2537 Å. This and the other inactivation curves in the diagram were determined by sowing equal, small, quantities of the well mixed and shaken culture on culture media and then exposing them to irradiation for different lengths of time. After the necessary incubation the percentage was counted of the bacteria not yet rendered inactive. This percentage has been plotted in the graph on a logarithmic scale against the dose of irradiation.

From left to right, the curves each relate to a more advanced stage in the ageing of the culture sown in the medium. It has to be taken that this suspension reached the logarithmic phase in two hours.

It appears that in the state of the strongly aged culture (dying-off phase) the bacteria are less sensitive to ultra-violet radiation than in the logarithmic phase.

For practical purposes the curves given in fig. 9 show that it is wise to be careful when quoting figures for doses and that it is well to bear in mind that bacteria, and micro-organisms in general, may be in a more or less resistant state.

In addition to the differences in sensitivity something can also be deduced from these curves about the mechanism of the inactivation.

In cases where bacteria were inactivated by electron rays and alpha rays it appeared that one ionization in a specific part of the bacterium suffices. Supposing that, in analogy therewith, absorption of one quantum is needed to bring about inactivation by ultra-violet irradiation, then the number of bacteria inactivated per unit of time is proportional to the radiation intensity I and to the number of active bacteria N, thus

$$\mathrm{d}N = -C\,N\,I\,\mathrm{d}t.$$

By integration we get the relation:

$$\log_e \frac{N}{N_0} = -C\,I\,t,$$

and the graphical representation gives a straight line, as in fig. 9 *IV*.

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[2]) B. Malmgren and C. G. Heden, Studies of the nucleotide metabolism of bacteria, Acta Path. Micr. Scand. **24**, 417, 1947.

It may be taken that the absorption must take place in that nucleoproteid system that performs an essential function in cell division. Owing to the absorption a mutation takes place in the system, viz. a lethal one, whereby the capacity of multiplication is stopped. If a biochemical foundation could be given for this conception it would be of the greatest importance for our knowledge of bacteria.

The non-linear trend of the curves for the other phases is an indication that in those phases the ultra-violet inactivation is of a more complex nature.

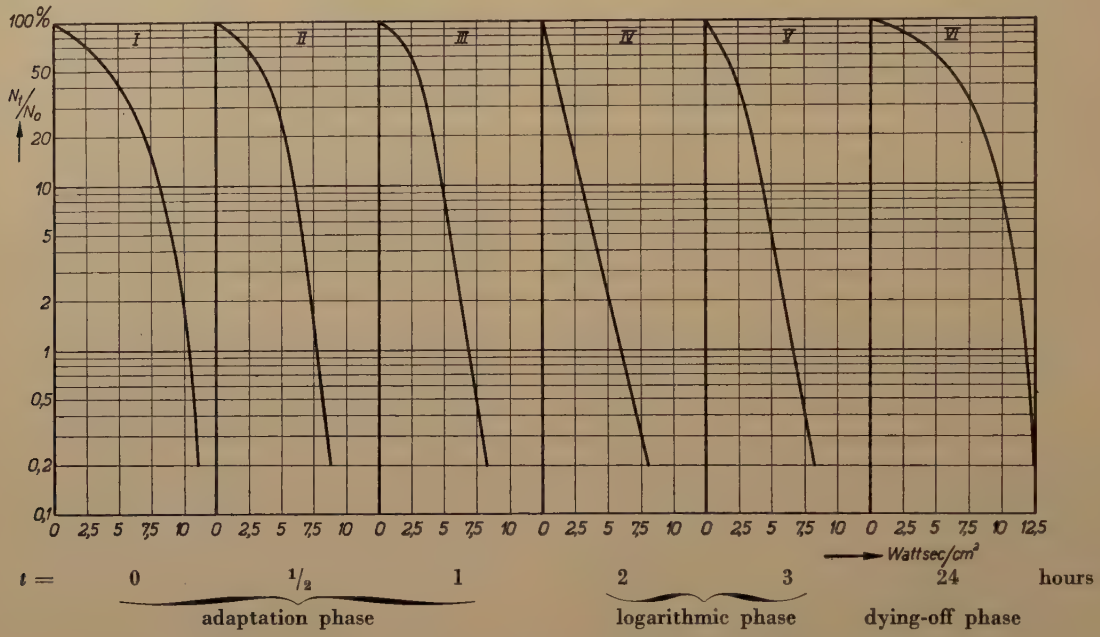

Fig. 9. Inactivation of coli bacteria in different life phases (*I* to *VI*) by irradiation with 2537 Å, as function of the dose (in wattsec/cm²). Along the ordinate the ratio of the number of bacteria not yet inactivated (N_t) to the original number (N_0). The dose as administered t hours after sowing the bacteria in the culture medium.

Influence of the nature of the medium

One of the most common applications of the germicidal lamps is for the sterilization of air, either stationary or in motion. Investigations have shown that the doses required to reach a certain degree of inactivation of germs in the air are very much smaller than those that follow from measurements taken in suspensions and from cultures on agar plates.

Experiments have been made with slow-moving currents of air irradiated with certain doses of ultra-violet, while at the same time parallel tests were carried out without irradiation. It was thereby possible to determine the dying-off rate as a function of the dose of irradiation for different micro-organisms introduced into the air by atomization of a suspension.

Whereas for Bacterium coli in an aqueous suspension a dose of about 10 mWsec/cm² was required to reduce the number of bacteria to 1 - 0.1%, in a suspension atomized into the air the same effect was reached with a dose of 1 mWsec/cm².

This phenomenon, so important for practical purposes, is usually ascribed to a change of the micro-organism after atomization in air. We are still in the dark about the physiological aspect of this change. There is, however, a purely physical factor to be considered when judging this difference, though it only partly explains it.

The fact is that when a liquid suspension is irradiated there is practically no diffraction or scattering of the rays on the surface of the bacterium, so that there is the same intensity everywhere inside the bacterium as in the surrounding liquid. In the case of a suspension atomized in the air it is to be presumed that owing to the curvature of the surface a certain lenticular action takes place along the boundary of the micro-organism, which action, however, cannot be calculated by geometrical-optical means because the dimension is only a few times that of the wavelength of the radiation used. Calculations made for the case of a spherical micro-organism indicate, while making allowance for interferential phenomena, that the intensity of radiation in the centre may be about twice that outside the organism.

Applications

In the application of ultra-violet sterilization there are two cases to be distinguished: volume sterilization and surface sterilization.

For microbiological manipulations, such as culture inoculations, it is often desirable to carry these out in germ-free surroundings, since in spite of the most rigorous sanitary measures it is not always possible to prevent germs being carried along by currents of air.

Sterilization can be carried out by direct irradiation of the space or place where sterile conditions are required, but this is only practicable when human beings are seldom present, because the radiation of 2537 Å has unpleasant (and in course of time injurious) effects upon the human organism. With a sufficient dose of the radiation painful erythema arises on the human skin, while, if the eye is exposed to the rays, a very troublesome, though harmless and quickly healing, inflammation of the conjunctive membrane arises (conjunctivitis).

For these reasons, in the U.S.A., where the germicidal lamp was first introduced, regulations have been laid down specifying the conditions that have to be complied with for safeguarding people in the vicinity of these lamps. Experience teaches that if these regulations are observed there is no risk of any harmful or troublesome consequences arising from the use of these lamps. It is specified, for instance, that the human skin must not be exposed longer than 7 hours per day to an intensity of at most 0.5 μW/cm^2 (for the wavelength 2537 Å). In cases of continuous irradiation (e.g. in hospital wards) the intensity on the skin must not be more than 0.1 μW/cm^2. It is the task of the designer of an installation employing germicidal lamps to make this action as effective as possible while duly observing the safety requirements.

In places where people are regularly present the lamps can be so mounted that only the upper part of the room is irradiated. The natural circulation of the air then ensures that all germs come to pass through an area of intense radiation. The lamps can be mounted in aluminium fixtures directing the rays upward, but care has to be taken that the ceiling does not reflect too much of the ultra-violet radiation, so as to avoid trouble from erythema and conjunctivitis.

As an example of indirect irradiation a case can be mentioned where a laboratory 15 m^2 in area and 4 m high had to be kept free of germs. On one of the walls at a height of 2 m a fixture was mounted with one TUV lamp. The result of the irradiation was investigated by determining the bacteria

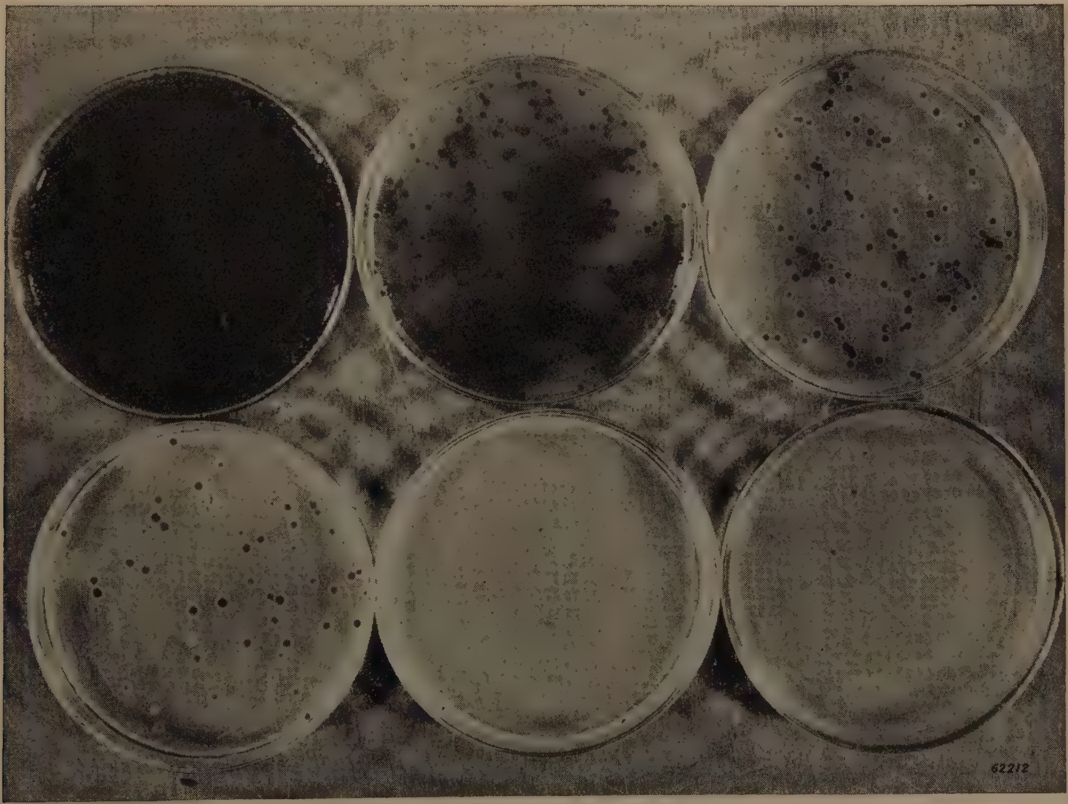

Fig. 10. Development of bacteria due to infection from the air. *Top row*: in a space where no lamp was burning, *bottom row*: germicidal lamp switched on immediately after atomization of bacteria in the air. From left to right: 2, 5 and 15 minutes after atomization.

content of samples of the air. After having atomized a culture of coli bacteria a certain quantity of air was collected with the aid of an apparatus whereby the air was blown onto a culture medium.

The result can be seen in *fig. 10.* The upper row gives an impression of the number of bacteria collected during the first 2, 5 and 15 minutes after atomizing and before the lamp was switched on. In the case of the second series of collections (lower row) the lamp was switched on immediately after the atomization, and it is seen that after 5 minutes no more bacteria were collected.

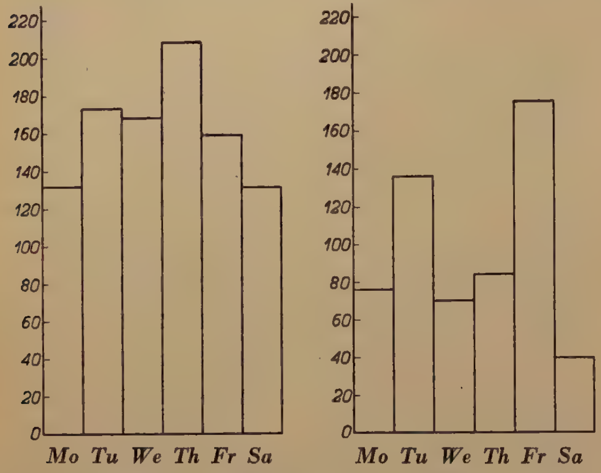

Fig. 11. Number of germs developed on a culture medium in Petri dishes in a busy, small office. On the left without TUV lamp, on the right with TUV lamp burning. From left to right the six working days in a week.

This result is not always to be expected, because as a rule bacteria from a young culture as used for this experiment have less resistance than the saprophytic micro-organisms present in large numbers in the air, and which are usually harmless. Pathogenic (disease-producing) bacteria and germs from scattered drops in the air are generally very soon killed. *Fig. 11* shows the result of irradiation in an office where there was a great deal of moving to and fro and where saprophytes were contained in the air. Several times a day for a fortnight the number of germs (bacteria and moulds) was determined that were collected in 5 minutes on a series of Petri dishes.

The graph on the left of fig. 11 represents the situation without the lamp burning, whilst that on the right shows the results with the lamp burning. There were still rather a large quantity of bacteria collected while the lamp was burning, but it may be taken that mainly the pathogenic bacteria had disappeared, so that the real effect is more satisfactory than would at first appear from the graph.

Often a more local sterilization of a certain area is required, as for instance on conveyor belts, in filling machines, washing machines, yeast vats or for inoculating cabinets in bacteriological laboratories, of which last-mentioned application a picture is given in *fig. 12.*

In the dairy industry previously sterilized tins are often transported over a rather long distance

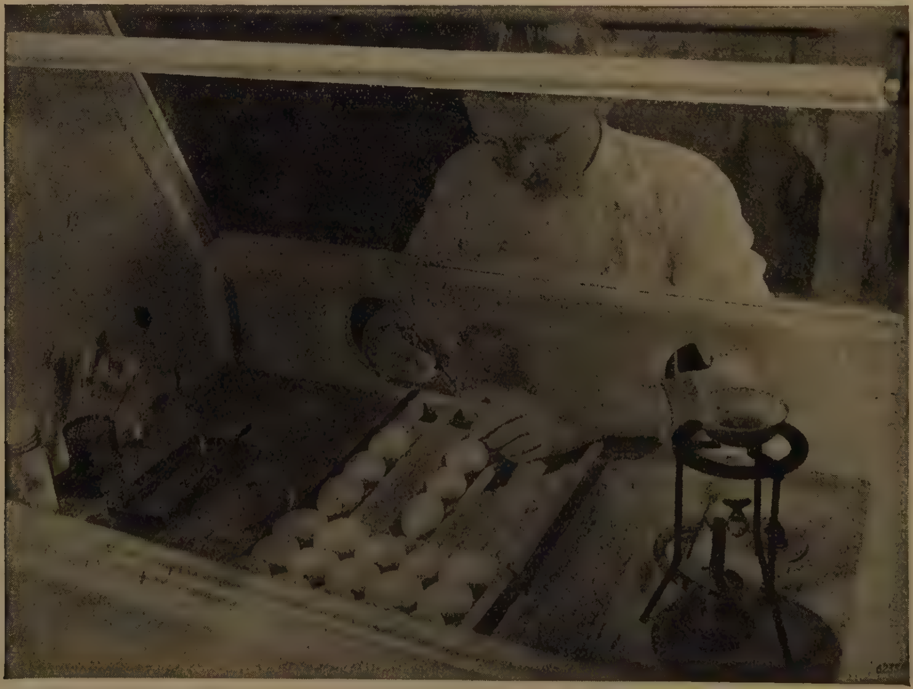

Fig. 12. Inoculating eggs with a highly infectious material, as carried out in the Institute for Tropical Hygiene at Amsterdam. The germicidal lamp is of particular importance here for safeguarding the laboratory workers.

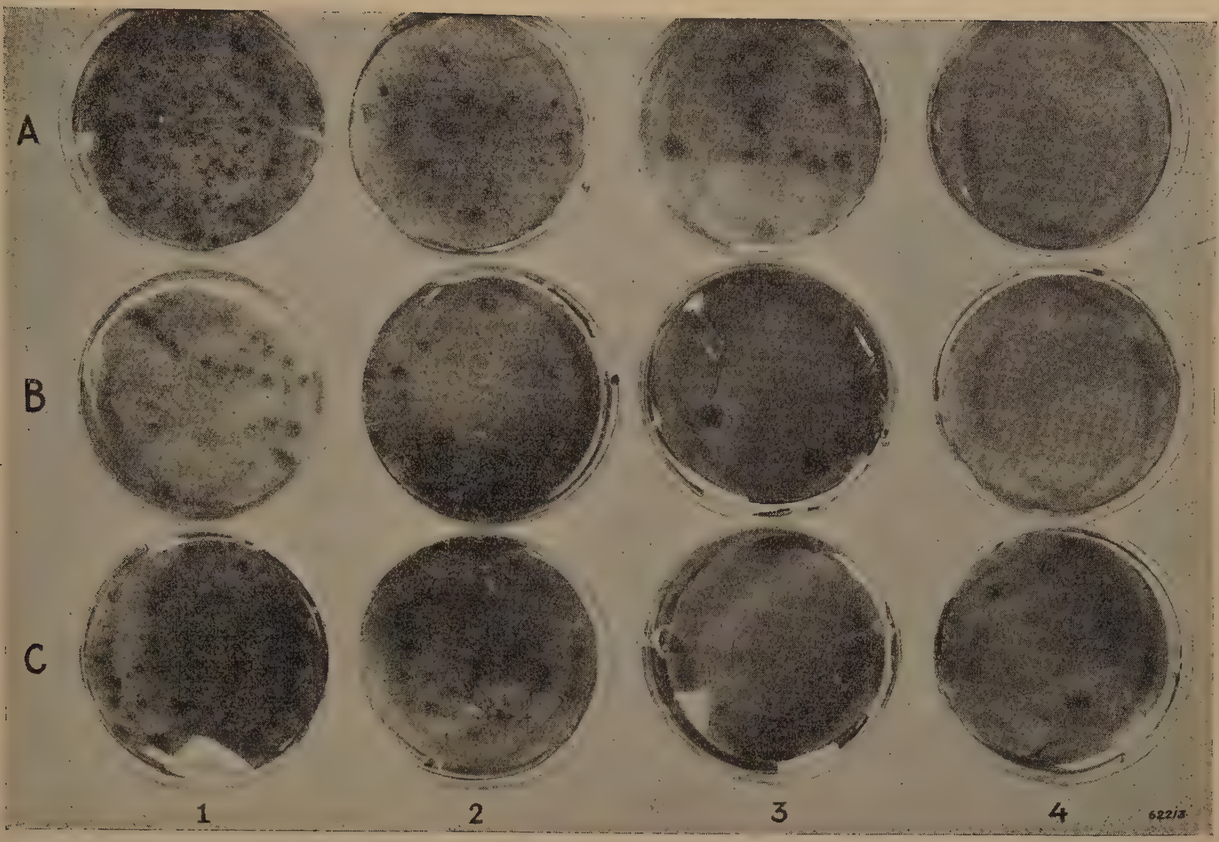

Fig. 13. Occurrence of bacteria and moulds on floors. A = covered with linoleum, B = tiled floor, C = parquet floor. *1* without cleansing, *2* irradiated, *3* after 3 minutes' vacuum cleaning, *4* irradiated after vacuum cleaning.

to the filling machines via conveyor belts, with the chance of infection from bacteria on the way. Here the solution is ready to hand by mounting a series of TUV lamps over the conveyor belt, so as to keep the tins sterile.

In laboratories an inoculating cabinet with a TUV lamp mounted inside it renders good service. As a special application may also be mentioned the use of the TUV lamp for preventing the growth of algae in hot-houses [3]).

Direct irradiation of surfaces has not always the desired result owing to the presence of dust, since in dust spores of bacteria and moulds are often surrounded by organic material, which intercepts the rays.

The effect can be investigated by using filter papers soaked in a suitable culture solution, say agar, pasted under sterile conditions on the surfaces to be tested. A large proportion of the germs present then stick to the agar and after "culturing" an idea can be formed of the vegetation on the paper, as shown in *fig. 13*. The first column on the left are specimens taken from a dusty linoleum-covered floor, a tiled floor and a parquet floor, while those in the second column show the result after direct irradiation of the same floors.

In practice the usual steps, like washing down, chemically disinfecting and vacuum cleaning, are taken. The effect of 3 minutes' vacuum cleaning is shown in the third column, where an appreciable reduction of the number of germs is already noticeable. It is therefore certainly advisable to make good use of a vacuum cleaner. In several cases it is warranted to follow this up with ultra-violet irradiation, as for instance over the floors of corridors in hospitals, of shower-bath cells, of doctors' waiting rooms, of polyclinics, where according to the manner in which it is applied ultra-violet irradiation may considerably reduce the number of germs. The fourth column of specimens in fig. 13 shows that then one may speak of almost perfect sterility.

Summary. Ultra-violet radiation of the wavelength 2537 Å has an "inactivating" action upon bacteria and moulds, the process of division being checked, so that no cell division takes place. As a source of this radiation a low-pressure mercury-discharge lamp, the TUV lamp, has been developed, with the aid of which it is possible to reduce considerably the number of germs in places where injurious consequences are to be feared. A dose of 5 mWsec/cm^2 is usually sufficient to render 90% of the irradiated bacteria inactive, the dose actually needed depending upon the species, the surroundings and the vital phase of the bacteria at the moment of irradiation.

When this lamp is employed for disinfecting rooms the fixtures must be of a suitable construction and mounted in such a way as to avoid harmful effects of the radiation upon persons present in the room.

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[3]) R. van der Veen, A small greenhouse with artificial lighting for studying plant growth under reproducible conditions, Philips Techn. Rev. **12**, 1-5, 1950 (No. 1).

SATURATION OF FLUORESCENCE IN TELEVISION TUBES

by A. BRIL and F. A. KRÖGER.

535.376:621.385.832

The picture observed on the fluorescent screen of the cathode-ray tube in a television receiver is not, as a rule, a faithful reproduction of the original. One of the causes of this, though of less importance than others, is the fact that the light from the fluorescent screen does not continue to increase proportionately with the intensity of the electron beam but shows what may be called saturation. This phenomenon of saturation is not usually noticeable, but in certain cases it may become very troublesome; it may cause changes in the colour of the fluorescent light with changing load. Investigations have shown how this deficiency can be overcome.

Introduction

In cathode-ray tubes, for instance in oscilloscopes and television receivers, and in the case of the electron microscope use is made of the fluorescence of certain solids [1]) when bombarded with electrons. In this article we shall deal with the fluorescing substances (phosphors) used in television tubes.

The use of phosphors for this purpose is made possible mainly on account of the fact that the fluorescence increases in intensity with the current density of the electron beam. So long as the latter is not too high, the intensity of the light increases in direct proportion with it, but when the electron beam is of high density the increase in the intensity of the light is less than proportional; in other words, the efficiency of the fluorescence decreases when the load is high. Eventually, if the density of the electron beam is increased still further, there is hardly any increase at all in the intensity of the light, and one then speaks of saturation.

This deviation from the proportionality between brightness and current density is one of the reasons why the intensities in the television picture are not proportional to the corresponding intensities in the original. This need not be troublesome. In fact also in an ordinary photographic print the intensities of the picture are not proportional to those of the original: in this case, too, "saturation" occurs, due — inter alia — to the simple fact that the brightness of the picture can never be greater than that of the unexposed white paper.

Disproportionality tends to become troublesome, however, when a fluorescent screen is used which, in order to produce a white picture, is composed of a mixture of two phosphors (say, one with yellow and one with blue fluorescence) which saturate at different current densities. When the light is of high intensity a change in colour then arises, which of course is undesirable.

When studying this complex of phenomena, which, for the sake of brevity, we shall refer to as "saturation", we have to distinguish between the case of continuous electron irradiation, where the density of current on all points of the screen is constant in time, and the case of discontinuous (scanning) irradiation, such as occurs when the screen of a television tube is scanned by a narrow beam of electrons tracing out a raster. Assuming, for the sake of simplicity, that the cross section of the electron beam is a square, and that this beam is made to scan the whole of the surface of the image in precisely contiguous strips, then the time average of the density of current is of the same value, $\bar{J}_d$, at all points of the screen, and this value corresponds to the current density in a continuous beam, J_c, which, given an equal total current, would cover the whole area of the screen. So long as $\bar{J}_d$ and J_c are not excessive, the brightness of the screen under continuous irradiation will then be equal to that under intermittent irradiation. The actual current density, J, in the case of intermittent irradiation however is many times greater than $\bar{J}_d$. If f is the image frequency and T the time the electron beam takes to scan a certain spot, i.e. the time taken for the beam to pass through a certain point on the screen, then

$$\bar{J}_d = f\,J\,T;$$

in most television receivers $f = 25$ or $30\ \mathrm{sec}^{-1}$, whilst T is in the order of 10^{-7} sec (see appendix). Thus J is a factor of about 3 to 4 times 10^5 greater than $\bar{J}_d$.

When studying this problem of saturation we shall be mainly concerned with the case of discontinuous irradiation, since this is most commonly met in practice. There are various reasons, however, why we should also consider the case of continuous irradiation. In the first place this is a theoretically simpler case and secondly continuous irradiation lends itself better to accurate experimentation. It must be borne in mind, however, that while two substances may behave exactly alike under scanning conditions, in the case of continuous irradiation they sometimes behave quite differently. An example of this is illustrated in *fig. 1.* We shall see that this is due to rather different factors prevailing in the two cases.

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[1]) The use of fluorescing substances has been discussed at length in an article by F. A. Kröger, Applications of luminescent substances, Philips Techn. Rev. 9, 215-221, 1947.

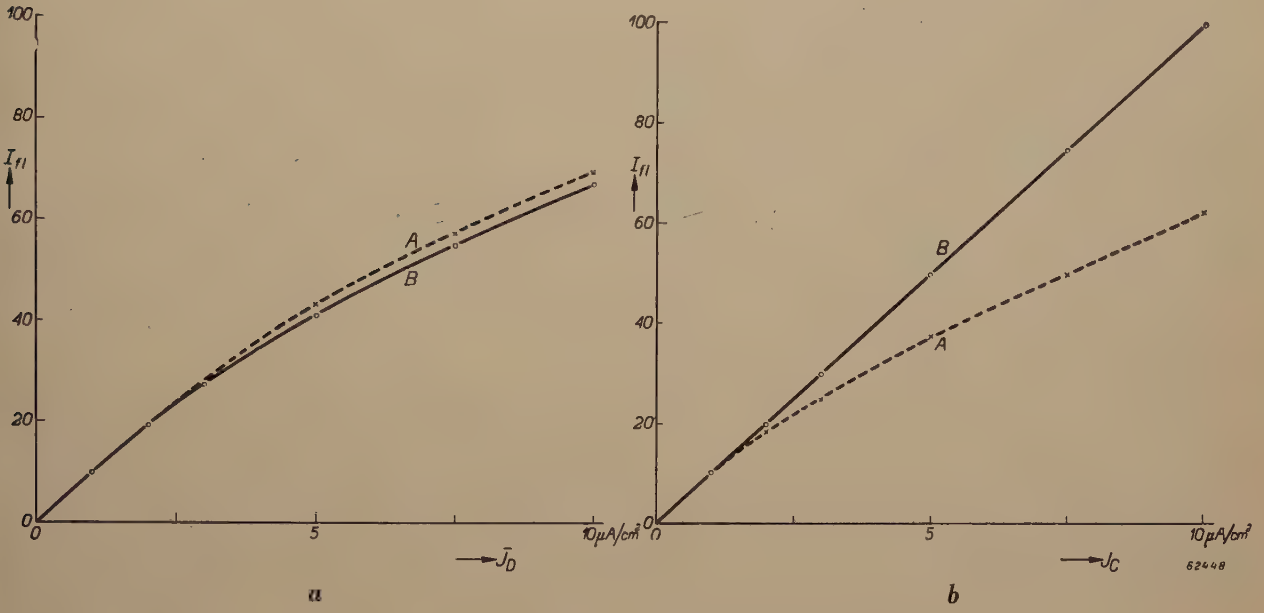

Fig. 1. *a*) Light output as function of the average current density for a zinc-silicate phosphor activated with manganese (*A*, Zn_2SiO_4 - 0,015% Mn_2SiO_4) and for a zinc-sulphide phosphor activated with silver (*B*, ZnS - 0.010% Ag), in the case of discontinuous irradiation. The two phosphors have about the same activator content and are saturated at the same average current density. *b*) Light output as function of the current density for the same phosphors as in (*a*) but for the case of continuous irradiation: it appears that the sulphide phosphor in this case does not reach saturation, whereas the silicate phosphor becomes saturated at the same current density as in the case of discontinuous irradiation. The light output has been plotted in arbitrary units, as applies also for the analogous following graphs.

Cause of saturation

The proportionality between the light output and the intensity of the electron beam is disturbed by an effect intimately related to the mechanism of fluorescence. This mechanism may be described as follows. When an electron travelling at a high velocity impinges on a crystal the energy of that electron is transmitted to a number of electrons in the crystal lattice, thereby exciting them to a state of greater energy. In most crystals the electrons excited in this way return to their original state without any emission, the excitation energy being converted into lattice energy, i.e. heat.

It is only in particular systems that the excitation energy is converted, at least in part, into fluorescence. In the case of most of these substances this is due to the presence of foreign atoms or groups of atoms (in small concentration) called activators. The excitation energy is partly transmitted to these activators, so that they in turn become excited. Sooner or later the activator centres resume their original state, this being accompanied by the emission of fluorescent light.

That part of the energy of the lattice electrons that is not transmitted to the activators is lost in the form of heat. Consequently the energy efficiency of the fluorescence must be less than 100%. The highest value reached in practice is about 20%.

Following this line of thought it can readily be understood that saturation is likely to take place. The greater the density of current, the more activators are excited. Now once an activator centre has been excited it cannot for the moment absorb more energy, since it requires some time to radiate that energy and return to its original state; the total number of centres present being naturally limited, at high currents there will be fewer centres available to which energy can be transmitted. Thus the energy of the excited lattice electrons is converted with lower efficiency into fluorescent light than is the case with lower current density.

There is another phenomenon affecting the proportionality between current density and light output: owing to bombardment by the electrons the fluorescent screen becomes heated. Now above a certain critical temperature the fluorescence of solids tends to decrease rapidly with rising temperature [2]). When that critical level is exceeded the light output does not increase with the current at the same rate as it does in the case of lower temperatures. This phenomenon can be avoided by choosing a phosphor that has the highest possible critical temperature. We cannot go into this further within the scope of the present article.

Theory of the saturation of fluorescence

In order to obtain an insight into the factors determining this saturation let us consider the energy levels of a fluorescent crystal such as are represented diagrammatically in *fig. 2* [3]).

The basic level is indicated by *0*, an excited level by *1*. Given a certain current density J of the electron beam, a number, I, of lattice electrons in the crystal are excited per second per unit volume. Except for extremely high currents, with which we are not concerned here, I is always directly proportional to J. The system may return from the level *1* to the level *0*, without radiation taking place; let the probability of this transition in the interval of time dt be equal to $a dt$ [4]). It may also happen that the system passes from the level *1* to a state *2* where part of the energy is transmitted to an activator centre and the latter thus becomes excited. The probability of such a process taking place in the interval of time dt is proportional to the number of activator centres not excited and thus can be represented by $\beta(N-n_2)dt$, where N denotes the total number of activator centres per volume unit, n_2 the number of excited centres per volume unit (thus $n_2 < N$) and β is a proportionality constant. The case where an activator centre is directly excited by an impinging electron is very rare and may be ignored. An excited centre returns to its original state with the emission of fluorescent light; let the probability of this transition taking place in the interval of time dt be γdt.

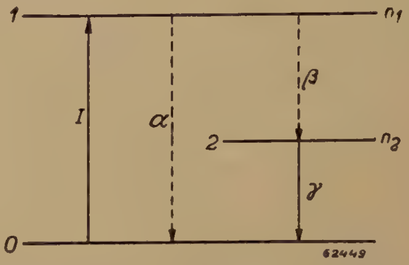

Fig. 2. Energy levels in a fluorescing crystal; *0* initial level, *1* excited level of the lattice, *2* state at which an activator is excited. The quantities a, β and γ determine the probabilities of the various transitions in the crystal. The occupation of the levels *1* and *2* is denoted by n_1 and n_2 respectively. Transitions without radiation are indicated by dotted lines.

The transition probabilities for the three processes mentioned are thus a, $\beta(N-n_2)$ — which quantity in the case of not too high a load is in the order of βN — and γ, respectively. In practice it is found that, to a close approximation, a and βN amount to at least 10^8 sec^{-1}. For the ratio of a to βN a figure greater than 3 is usually found. The constant γ may differ considerably from one phosphor to another; taken on the whole it lies between 10^2 and 10^6 sec^{-1}. The reciprocal value $1/\gamma$ of this constant is the average lifetime, τ, of an excited activator centre; τ thus varies between 10^{-2} and 10^{-6} sec.

Denoting the occupation (per volume unit) of the level *1* by n_1 and that of the level *2* by n_2, the change of n_1 and n_2 with time can be formulated by the differential equations:

$$\frac{dn_1}{dt} = I - an_1 - \beta n_1 (N-n_2), \quad . \quad . \quad (1)$$

$$\frac{dn_2}{dt} = \beta n_1 (N-n_2) - \gamma n_2 . \quad . \quad . \quad . \quad . \quad (2)$$

After what has already been said there will be no ambiguity about the meaning of the various terms. It only remains to add that the term γn_2 in (2) represents the number of light quanta emitted per second per unit of volume. It is therefore important to know how n_2 behaves as a function of the number of lattice electrons I excited per second and of the time t, bearing in mind the distinction that has to be made between continuous and discontinuous irradiation. The manner in which this behaviour is calculated is explained in the appendix. The results are as follows.

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[2]) See F. A. Kröger and W. de Groot, Influence of temperature on the fluorescence of solids, Philips Techn. Rev. 12, 6-14, 1950 (No. 1).

[3]) For an extensive mathematical treatment of saturation see A. Bril, On the saturation of fluorescence with cathode-ray excitation, Physica, The Hague 15, 361-379, 1949 (No. 3/4).

[4]) It is assumed that this is a "monomolecular" process, i.e., that the probability for a transition is proportional to the first power of the occupation of the level *1*. The "bimolecular" case, where we have to do with a recombination of electrons and "holes" (see the articles quoted in footnotes [2]) and [3])) and the probability of a transition taking place is proportional to the square of the occupation of level *1*, is left out of consideration here.

For the case of continuous irradiation, the relation between I and the number of fluorescent quanta L_c emitted per second per unit of volume is found, to a good approximation, to be:

$$L_c = \gamma n_2^* \approx \frac{\eta_0 I}{1 + \eta_0 I/\gamma N} \quad . \; . \; . \; . \quad (3)$$

where n_2^* represents the constant ultimate value of n_2 when the irradiation has lasted some time, and η_0 is the quantum efficiency of the fluorescence at a low current density, i.e. the number of light quanta emitted per excited electron in the original lattice. This quantum efficiency η_0 is given by

$$\eta_0 = \frac{\beta N}{a + \beta N} . \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

Henceforth we shall assume that $a/\beta N \approx 10$, so that $\eta_0 \approx 0.1$.

From (3) it is seen at once that the proportionality between L_c and I begins to be disturbed as soon as the term $\eta_0 I/\gamma N$ in the denominator — which at low load is $\ll 1$ — approaches the value 1, thus when I becomes so great as to satisfy the condition

$$\eta_0 I \approx \gamma N = N/\tau \, . \quad . \; . \; . \; . \; . \quad (5)$$

For the case of discontinuous irradiation the intensity of the light depends also upon the time T the electron beam takes to scan a certain spot. Since T is much smaller than τ, no stationary state will be reached. For the average number of quanta $\overline{L}_d$ emitted per second we therefore find a different expression, viz., to a close approximation:

$$\overline{L}_d \approx fN\,(1 - \mathrm{e}^{-\eta_0 IT/N}), \quad . \; . \; . \quad (6)$$

where f = the image frequency. Introducing the time average of the number of excited electrons $\overline{I} = fIT$ we get the formula

$$\overline{L}_d \approx fN\,(1 - \mathrm{e}^{-\eta_0 \overline{I}/fN}) \, . \quad . \; . \; . \; . \; . \quad (6a)$$

In this case there will be a deviation from the proportionality between $\overline{L}_d$ and $\overline{I}$ as soon as $\eta_0 \overline{I}/fN = \eta_0 IT/N \approx 1$, thus when

$$\eta_0 \overline{I} \approx fN \quad \text{or} \quad \eta_0 I \approx N/T, \quad . \; . \; . \quad (7)$$

which result may be compared with formula (5).

In the above results *no* account has been taken of the effect of quenching centres, i.e. centres of the same nature as activator centres but having the property of returning to the original state from the excited state without emission. For the purpose of our investigation this omission is allowed because we are assuming for the time being that the concentration of activator centres is much greater than that of quenching centres. We shall revert to the quenchers later.

Comparison between continuous and intermittent irradiation

To compare the saturation taking place with one and the same phosphor in the case of continuous irradiation with that in the case of discontinuous irradiation the light intensity can be plotted as a function of the current density in the one case and as a function of the average current density in the other. The curves thus produced are called characteristics. From equation (3) it follows that with continuous irradiation the number of light quanta emitted per unit of volume per second approaches γN if the current density is allowed to increase indefinitely. With intermittent irradiation it follows from (6a) that the limit for the number of light quanta in this case is equal to fN (assuming f to be smaller than γ). For small values of the current density the number of quanta emitted is equal (see above). When the two characteristics are reproduced in one graph (*fig. 3*) we thus find two curves which have the same initial slope

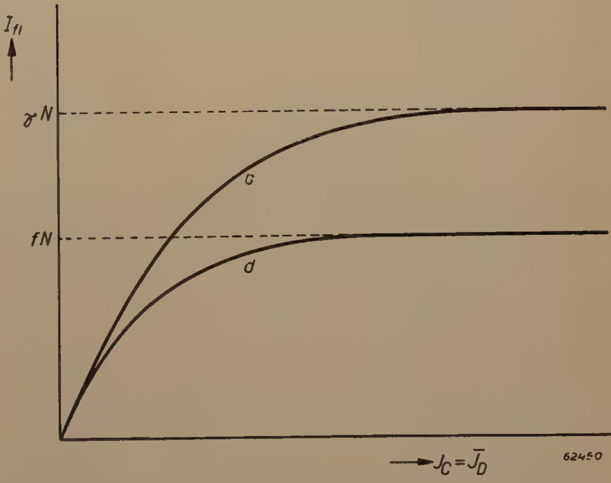

Fig. 3. Comparison of the characteristics of one and the same phosphor under continuous irradiation, curve *c*, and under discontinuous irradiation, curve *d*. Plotted on the same scale as abscissa is the current density and the average current density in the beam respectively.

but a different "ceiling", namely γN for the case of continuous and fN for the case of scanning irradiation.

The image frequency f in British television receivers is equal to 25 sec^{-1}; as we have already seen, γ may vary between 10^2 and 10^6 sec^{-1}. A phosphor with a high γ-value (short lifetime of the excited centres) will behave quite differently from one with a low γ-value. If the quotient γ/f is in the order of unity, as is the case with the lowest values of γ, such as may occur with silicate phosphors activated with manganese, then the "ceiling" is of about equal height for both curves and, hence, if under scanning conditions saturation becomes noticeable with a certain J_d, then under continuous irradiation saturation will likewise occur with an approximately equal value of J_c. But when $\gamma \gg f$, as is the case with many sulphides, for instance those activated with silver ($\gamma \approx 10^5$), the ceiling for continuous irradiation may be a factor 1000 higher than that for scanning conditions. In that case, in the range of current densities where saturation becomes noticeable under intermittent irradiation, there will be no sign of any deviation from the proportionality under continuous irradiation. To carry out experiments regarding saturation also for the case of continuous irradiation a 1000 times greater current density would be needed, which is not practicable.

Comparison of the characteristics of two phosphors

In order to compare the fluorescence of two different phosphors, e.g. under scanning conditions, the two characteristics can again be plotted in one graph. To be able to judge at once any difference in saturation, the initial slopes of the two curves can be made to coincide by enlarging the scale for the ordinate of one curve by a factor equal to the ratio of the initial efficiencies of the two phosphors. The curve which, after this transformation, has the lowest ceiling corresponds to the phosphor showing greatest saturation.

For discontinuous irradiation this saturation is governed entirely by fN, and thus, since with a given television system f is a constant, by N. Phosphors with a high N-value (large activator content) will therefore have less tendency towards saturation than those with a small N-value. In its generality this conclusion holds equally for a comparison of two phosphors under continuous irradiation, but in this case the saturation is governed by the factor γN, thus being dependent upon γ in addition to N; two phosphors with about the same activator content but with different γ-value will thus differ in saturation, that having the greater γ-value showing the less saturation.

Experimental results

Following upon the theoretical considerations derived in the foregoing, we shall now discuss some experimental results. First of all we must account for the difference in behaviour of the two phosphors in fig. 1. From the fact that the two curves in fig. 1*a* practically coincide it follows that for the two phosphors in question the number of fluorescent centres per volume unit must be about equal (still disregarding the effect of quenchers), whilst the marked difference between the curves in fig. 1*b* points to a considerable difference in the value of γ. And indeed the value of τ for the silicate phosphor *A* is about 10^{-2} sec, whilst the lifetime of the excited centres in the case of the sulphide phosphor *B* is about 2×10^{-5} sec. Consequently *A* will very soon show saturation under continuous irradiation, whereas with the same current *B* will show practically no saturation at all.

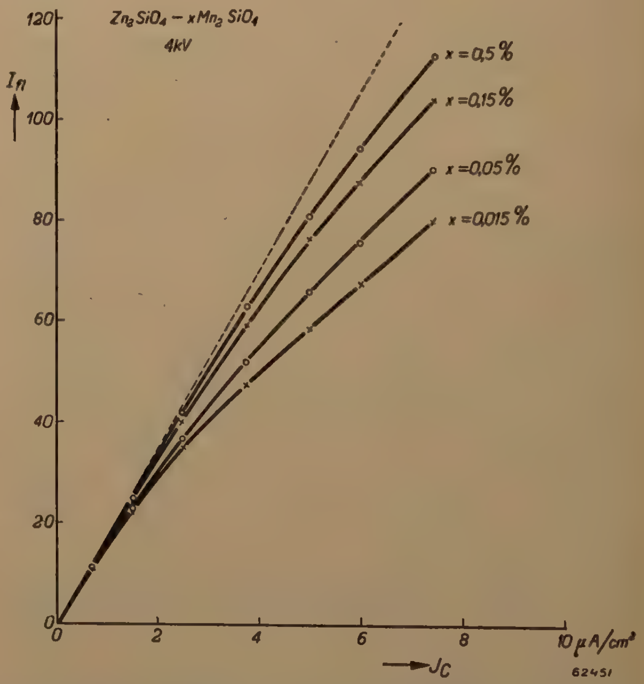

Fig. 4. Characteristics for continuous irradiation of a number of zinc-silicate phosphors activated with manganese. Saturation diminishes with increasing activator content. The characteristics have been brought to the same initial slope.

Since the value of γ ($\approx 10^2$) for *A* is comparable to that of f (= 25) the saturation of *A* under continuous irradiation will become noticeable with about the same current density as in the case of discontinuous irradiation (plotting the intensity of light against the average current density J_d and comparing the curves for the same number of μA/cm²).

The influence of the concentration of activators, thus of N, upon saturation is clearly seen from *fig. 4*, where the characteristics have been plotted for a number of silicates activated with different quantities of manganese. Since γ is practically independent of N, here N is the only variable. It is seen that the characteristic of the phosphor indeed becomes less curved as the concentration of activators increases (increasing manganese content).

For application in television cathode-ray tubes a number of phosphors are available to choose from. The most important are the zinc and zinc-cadmium sulphides and sulphoselenides activated with silver, and the zinc, zinc-beryllium and calcium-magnesium silicates activated respectively with manganese and titanium. The sulphides have a small activator content (about 0.01%) but a high efficiency (about 15 to 20%), whereas the silicates have a much larger activator content (0,1 to 2%) but a lower efficiency (about 7%). For applications where saturation is not likely to occur, as in the case of direct-vision television tubes, sulphides will therefore be mostly used. In projection-television tubes — these are small tubes with very high luminosity of the picture which can be magnified for projection onto a screen[5]) — the load is so heavy that the avoidance of saturation is more important than a high efficiency at a small current density, and it is for this reason therefore that silicates are used in these tubes.

Mutual matching of the characteristics of the components of a mixed phosphor

The white colour of the fluorescence in television tubes is usually obtained with the aid of a mixture of two phosphors, one with a blue and the other with a yellowish-green fluorescence. It is then necessary that under scanning conditions the colour of the screen remains the same for any current density, which means to say that the ratio of the intensity of the blue light to that of the yellow light must be practically constant. This implies that when the initial slopes of the two characteristics are made equal the curves must exactly coincide one with the other. If this condition is satisfied the characteristics are said to be uniform. A mixture of two phosphors not having uniform characteristics will show a fluorescence varying in colour with the intensity of the irradiation as soon as the latter becomes so great that one of the phosphors begins to show saturation. There is not much risk of this occurring with a silicate mixture, which has little tendency towards saturation, but it must certainly be taken into account in the case of a sulphide mixture or a mixture of a sulphide and a silicate.

Let us suppose that we have a white-fluorescing mixture of phosphors composed of a blue-fluorescing zinc sulphide activated with silver and a yellow-fluorescing zinc-cadmium sulphide activated with silver. The "yellow" phosphor usually tends towards saturation at a smaller average current density than the "blue" one. How, then, can the shape of one of the characteristics be so altered as to reach uniformity? This can be done in three ways:

1) Increasing the concentration of activators in the yellow component, thus raising the ceiling of the yellow characteristic to a higher level. There is a limit, however, to which one can go in this direction, because the efficiency of the phosphor reaches a maximum at a certain concentration of activators. Moreover, the solubility of the activator atoms in the crystal lattice is limited. Therefore not very much can be achieved by this method, in a general way of speaking.

2) Reducing the concentration of activators in the blue component, thus lowering the ceiling of the blue characteristic. Reduction of the activator concentration has scarcely any influence on the efficiency of fluorescence under low load. It is only with the very smallest activator concentrations that the initial efficiency is lowered, and then either the concentration is so small as to cause saturation to occur already with low intensities of the irradiation, or else it becomes of the same order as the concentration of the quenching centres, which as a rule are present only in a small concentration. The following table shows the effect of the activator content on the initial efficiency for the case of a zinc-sulphide phosphor activated with silver (voltage across the cathode-ray tube 10 kV).

Activator content in atomic percent.	Initial efficiency in percentage
1×10^{-2}	22
6×10^{-3}	22
4×10^{-3}	22
1×10^{-3}	18

In *fig. 5* an example is given of the matching of two characteristics by the method of reducing the activator concentration in the less saturating component.

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[5]) Cf J. de Gier, Projection-television receiver, II. The cathode ray tube, Philips Techn. Rev. **10**, 97-104, 1948.

When applying this matching method care has to be taken to avoid the occurrence of self-activation, by which is meant counteraction of the reduction of the activator concentration by formation of new activator centres by the atoms of the crystal lattice itself; when this arises there is hardly any change in the total concentration of activators. Self-activation can be avoided by applying a special method of preparation.

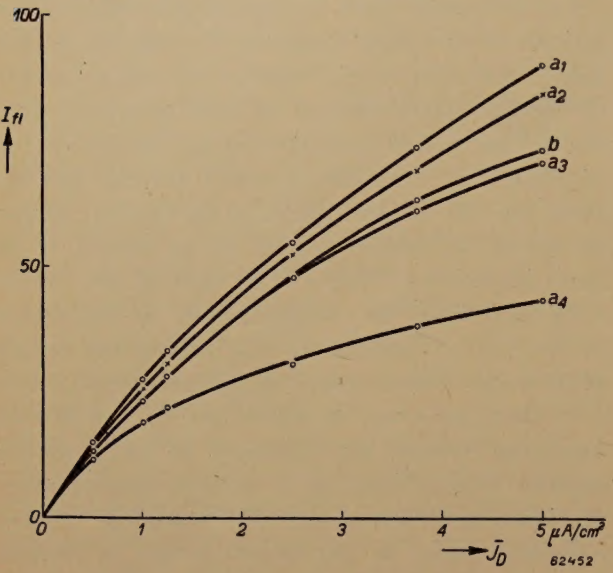

Fig. 5. Matching characteristics by reducing the activator content in the less saturating component. a_1, a_2, a_3 and a_4: characteristics of ZnS-xAg (blue) in which x = 0.01, 0.006, 0.004 and 0.001 atomic percent; b = characteristic of (Zn,Cd)S-Ag (yellow).
Matching is best when $x \approx 0.004\%$. The curves have been brought to the same initial slope.

3) Adding extra quenching centres in the lattice of the yellow component. A considerable portion of the energy otherwise almost entirely taken up by the activators when there are few quenching centres is then absorbed by the quenchers and as a result the intensity of the fluorescent light is reduced; thus the efficiency η_0 of the fluorescence is lowered. With intensities of irradiation leading to saturation in the absence of quenchers there will then be correspondingly less tendency towards saturation. This all finds expression in a flatter but straighter curve of the characteristic. However, even with the addition of quenchers, saturation ultimately sets in when a certain intensity of irradiation is reached, since the ceiling of the characteristic of course remains the same, namely fN.

Obviously this addition of quenchers does more harm than good. The efficiency at low intensities of irradiation usually drops so much that this method of matching the characteristics will only be applied in cases where no more than a slight correction is desired. An example of what can be achieved with this method is given in *fig. 6*; by the addition of 0.005% nickel to the yellow-fluorescing phosphor the efficiency at low load is reduced from 15% to 3%. It goes without saying that in order to maintain the white colour of the blended light, relatively more of the "yellow" phosphor has to be added.

Change of colour with defocusing of the electron beam in television tubes

Finally a phenomenon which may be noticed in the case of discontinuous irradiation of the television screen must be discussed. When the characteristics of the two components of a white-fluorescing mixture are uniform and thus under high load both components are equally saturated and no change takes place in the colour, colour-changes may still occur when the electron beam is defocused. Such is the case, for instance, when a blue-fluorescing calcium-magnesium silicate activated with titanium is mixed with a yellow-fluorescing zinc-beryllium silicate activated with manganese: when the beam is defocused while scanning the screen under high load the colour assumes a more bluish tint. At first sight one would be inclined to attribute this to an earlier saturation of the blue component, but since the characteristics are uniform this cannot be the cause. The explanation is as follows.

As already observed, we are dealing here with a case where the irradiation is discontinuous. Assuming that with the beam properly focused the lines of the raster do not partly overlap, then a certain spot on the screen is irradiated once every 0.04 sec. When the beam is defocused the lines will overlap, with the result that instead of the electron beam striking a certain spot once in each complete scanning it strikes that spot several times in succession at intervals equal to the time in which the beam traces a line of the raster, in our case about 10^{-4} sec.

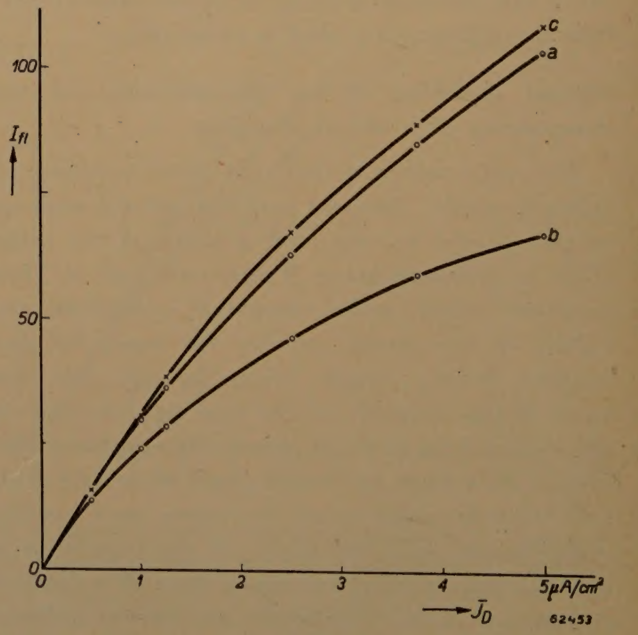

Fig. 6. Matching of characteristics by adding quenchers. The characteristic a of ZnS-0.01% Ag (blue) coincides almost with curve c, the characteristic of (Zn,Cd)S-0.01%Ag-0.005% Ni (yellow). In the absence of nickel as quencher in the latter phosphor the yellow characteristic, curve b, deviates considerably from the blue one. All curves have been brought to the same initial slope.

Since the blue component of the phosphor mixture has a τ-value of 2.5×10^{-5} sec, practically all the activator centres of this phosphor will again be in their original state each time the defocused beam crosses the spot considered, as represented in *fig. 7a*. The τ-value of the yellow component, however, is about 0.006 sec, which means that in 10^{-4} sec the number of activator centres excited by the previous passage of the electron beam is not appreciably reduced. Such is illustrated in fig. 7*b*. The consequence of the difference in τ will be that, when the electron beam reaches the intensity at which, with proper focusing, both components show saturation, in the case of defocusing of the beam the saturation of the blue component will be reduced but not, or scarcely so, that of the yellow component. As a result the colour of the fluorescence assumes a more bluish tint.

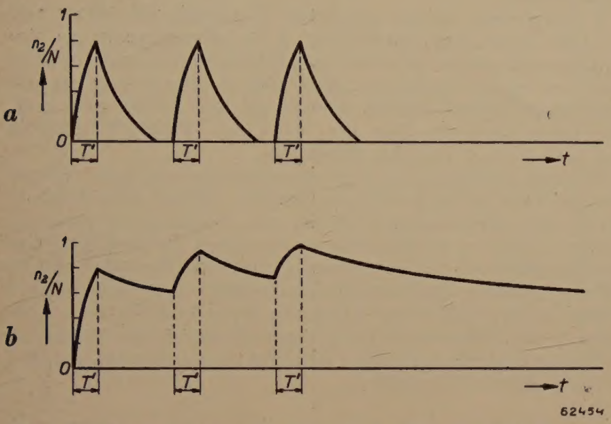

Fig. 7. When the electron beam in a television tube is slightly defocused a certain point on the fluorescent screen is irradiated not once during the scanning of the whole of the screen but several times in succession, each time a new line is traced. The variation of the number of excited activator levels as a function of time is indicated, for the case of three successive passages during a scanning, *a*) when the average lifetime of the excited levels is shorter than the interval of time between two successive passages (in our case about 10^{-4} sec), *b*) when it is longer than that interval. T' is the time the widened electron beam takes to scan a certain spot of the screen.

This can be confirmed by taking a look at the fluorescent screen under a high load through filters passing either blue or yellow light. When a blue filter is used the intensity of the light diminishes considerably during focusing, whereas with a yellow filter the reduction is only small. The fact that some reduction does indeed take place is due to the interlacing of the raster in the case of television tubes; owing to two adjaccent lines not being traced in one single scanning, part of the defocused beam may still strike yellow activator centres that have not been excited. (Of course this applies only when there is not too much defocusing.)

The foregoing phenomenon would seem to be contradictory to our earlier statement that in the case of intermittent irradiation the saturation is independent of τ. In our explanations concerning this case, however, it was assumed that the time elapsing between two successive passages of the electron beam is long compared with the duration of this decay time, a condition which is not complied with in the above example for the yellow component.

Appendix: Derivation of the formulae (3) and (6)

When a phosphor is subjected to a continuous electron bombardment in course of time a stationary state will be eached; there is then no further change in the occupation of the levels and n_1 and n_2 assume constant values which we shall denote by $n_1{}^*$ and $n_2{}^*$. Since the differential quotients in the left-hand members of (1) and (2) may be taken as equal to zero, we have

$$I - \alpha n_1{}^* - \beta n_1{}^* (N - n_2{}^*) = 0\,, \quad \ldots \quad (8)$$

$$\beta n_1{}^* (N - n_2{}^*) - \gamma n_2{}^* \quad = 0\,. \quad \ldots \quad (9)$$

For the number of fluorescence quanta emitted per second and per unit of volume we find:

$$L_c = \gamma n_2{}^* = \frac{I}{\dfrac{\alpha + \beta N}{\beta N} + \dfrac{\alpha}{\beta N}\,\dfrac{n_2{}^*}{N - n_2{}^*}}\,. \quad \ldots \quad (10)$$

The ratio L_c/I represents the quantum efficiency, i.e. the number of quanta emitted per excited electron. With a small current density, thus small $n_2{}^*$, this efficiency is

$$\eta_0 = \frac{\beta N}{\alpha + \beta N}\,,$$

with which formula (4) has been derived. As already stated, it is taken that $\alpha/\beta N \approx 10$; by ignoring a negligible quantity in (10) we find formula (3):

$$L_c = \frac{\eta_0 I}{1 + \eta_0 I/\gamma N}\,.$$

In the case of discontinuous irradiation, as occurs in television tubes, such a simple mode of reasoning is not possible. Let us suppose, for the sake of simplicity, that the scanned part of the screen is a square. The picture is divided into m contiguous strips. If the cross section of the beam is a square the whole area of the picture will therefore consist of m^2 picture elements of the size of that cross section. Per second the beam passes over fm^2 picture elements (f being again the image frequency), so that the time the beam takes to scan a certain spot of the screen is $T = 1/fm^2$ sec. If, for example, $m = 625$ and $f = 25$ sec^{-1}, then $T \approx 10^{-7}$ sec.

It is obvious that in this interval of time, which is very short compared with the lifetime τ of the excited activator centres, no stationary state is reached in the irradiated phosphor. In order to ascertain the behaviour of the phosphor we must therefore first consider the variation of n_2 with time. In principle this is possible by eliminating n_1 from (1) and (2), but the result cannot be written in a concrete form.

The solution of the equations (1) and (2), however, can be appreciably simplified, without seriously affecting the correctness of the conclusions, by ignoring in (1) the quantity n_2 with respect to N. For n_1 we then find

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = I - (\alpha + \beta N)\, n_1\,,$$

with as solution:

$$n_1 = \frac{I}{\alpha + \beta N}\left(1 - \mathrm{e}^{-(\alpha + \beta N)t}\right).$$

Thus it is seen that n_1 assumes a stationary value in a very short time ($\approx 10^{-8}$ sec). (Considering that after this short time level *2* will not by any means be filled, the fact of n_2 being ignored in equation (1) will not have been of any great consequence.) Introducing the stationary value in (2), then, in view of (4), we get:

$$\frac{\mathrm{d}n_2}{\mathrm{d}t} = I\eta_0 - \left(\frac{I\eta_0}{N} + \gamma\right) n_2\,, \quad \ldots \quad (11)$$

the solution of which is:

$$n_2 = \frac{I\eta_0}{\frac{I\eta_0}{N}+\gamma}\left[1-e^{-\left(\frac{I\eta_0}{N}+\gamma\right)t}\right] \quad . \; . \; . \; . \quad (12)$$

Thus we have found the relation between n_2 and t.

We now have to find the number of light quanta emitted by the phosphor as an average per second and per unit of volume.

When the beam has passed the element of the screen considered, thus at the moment $t = T$, the number of excited centres per unit of volume is equal to $n_2(T)$. Sooner or later, on an average after an interval of time τ, all these centres will emit a quantum. The number of light quanta per current impulse can thus simply be taken as equal to $n_2(T)$, and the average number of light quanta per second is equal to

$$\overline{L}_d = f n_2\,(T)\,.$$

(Actually the total number of quanta emitted per impulse is

$$n_2\,(T) + \gamma \int_0^T n_2 \mathrm{d}t\,.$$

The last term represents the number of quanta already emitted in the interval of time $0 < t < T$. This, however, is now smaller than $\gamma T \times n_2(T)$ and, since γT is usually $\ll 1$, namely $10^{-5} < \gamma T < 0.1$, the second term may be ignored.)

Hence we find:

$$\overline{L}_d = f n_2(T) \approx f \frac{\eta_0 I}{\gamma + \eta_0 I/N}\left[1 - e^{-\left(\frac{\eta_0 I}{N}+\gamma\right)T}\right].$$

Since $\gamma T \ll 1$, in view of (7) this may to a sufficient approximation be replaced by formula (6).

Summary. In the case where phosphors are brought to fluorescence by excitation with electrons, when a high current density is reached in the electron beam the efficiency of the fluorescence is found to decrease. This is due to the number of activator centres present in the crystal lattice being limited This "saturation" of the fluorescence appears, in the case of continuous bombardment with electrons, to depend both upon the activator concentration and upon the average lifetime of the excited activators. In the case of discontinuous irradiation, as takes place when the screen of a television tube is scanned with an electron beam, there is no longer any dependency upon the average lifetime of the activators if that lifetime is shorter than the interval between two successive passages and longer than the time the electron beam takes to scan a certain spot.

A comparison of the properties of silicate phosphors and sulphide phosphors shows that it is advantageous to use sulphide phosphors in tubes in which not too large current densities occur, whilst in tubes with a heavy load on the fluorescent screen silicate phosphors are to be preferred, notwithstanding the fact that as a rule their efficiency is less than that of sulphide phosphors.

In order to avoid a change in colour under a high current density when using a white-fluorescing mixture of two phosphors, the characteristics of the two components must be uniform. Various possibilities are discussed for matching the characteristics of the components one with the other. Even when a mixture with uniform characteristics is used colour-changing may still occur when the beam is defocused. This is due to the difference in the average lifetime of the activators in the components compared with the time taken for one line of the picture to be traced.